STUDIES ON TREATMENT AND DISPOSAL OF INDUSTRIAL WASTE

SUMMARY

THESIS SUBMITTED FOR THE AWARD OF THE DEGREE OF
Doctor of Philosophy
IN
APPLIED CHEMISTRY

BY
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ALIGARH (INDIA)
2000
Environmental pollution is an outcome of the direct activities of man. In a quest of improving his standard of living, man has 'perhaps' forgotten the consequences of going against nature. But he is now realising and hence the feeble call back to nature is now gaining momentum. Human happiness is more important than the luxuries provided by the modern civilisation.

Millions of tonnes of toxic and objectionable material is daily being disposed of in the environment as a result of industrial effluents being literally dumped in the atmosphere, soil and water.

Water pollution due to toxic heavy metals has been a major cause of concern to Engineers and Scientists. Several mishaps due to heavy metal contamination in aquatic environment increased the awareness about heavy metal toxicity. Among these, Minameta tragedy in Japan due to mercury poisoning ((1953-1960) and Itai-Itai' disease in Japan due to cadmium toxicity (1947) are well known.

Attention has been paid to the development of methods for many years for the removal of heavy metals and organic compounds from wastewater arising from industrial operations, particularly in the treatment of mine drainage waters spent solutions or effluents from extractive metallurgy processes, electroplating plants and other metal treatment or finishing operations. Conventional methods of heavy metal and organic compounds treatment in general perform satisfactorily to meet direct discharge requirements. The most common method for removal of heavy metals involves hydroxidee precipitation, on the basis
of its performance and ease of operation. Other available methods include evaporation, ion exchange, adsorption, electrodialysis, electrolytic extraction, reverse osmosis, but many of them are used in special circumstances because of their relatively high cost.

In recent years the adsorption technique for the removal and recovery of heavy metals and organic compounds from wastewater has received a great deal of attention. Activated carbon is the most common commercial adsorption medium and full scale processes based on this are in operation in developing countries. But, use of activated carbon is not suitable for developed countries like India, because of its high cost. It is therefore, felt after the exhaustive survey of literature on treatment technologies particularly upon adsorption that there is a necessity for inexpensive alternatives like low cost adsorbents for the removal of heavy metals and organic compounds from wastewater.

The work described in this thesis deals with the removal and recovery of heavy metals and organic compounds from aqueous solution and electroplating wastewater using various low cost and easily available materials as adsorbents.

This thesis comprises of five chapters:

**Chapter 1** is the introductory part giving a general idea regarding environmental pollution and nature and characteristics of industrial effluents and other objectionable material in the environment and emphasises its control. It describes the environmental pollution and its classification. It also details heavy metal pollution and organic
compounds and their sources. Besides, it provides the information regarding the composition of electroplating waste water. The studies carried out on removal and recovery of heavy metals by applying various conventional methods have also been discussed in literature survey.

Chapter 2 deals with the desorption studies and the removal of Zn(II) using Teak leaves (Tectona grandis) as adsorbent. The adsorption of metals from aqueous solutions and electroplating waste containing Zn(II) on teak leaves have been studied by batch as well as column process. The maximum adsorption (100%) is observed at 20 mgL⁻¹ initial Zn(II) concentration. Adsorption increases with increase in temperature. Thermodynamic parameters such as free energy (ΔG⁰), enthalpy change (ΔH⁰) and entropy change (ΔS⁰) were also calculated. Appreciable amount of Zn(II) is adsorbed in the pH range 2-6. The % adsorption increases as the adsorbent dose is increased. It may be concluded that by increasing the adsorbent dose the removal efficiency of teak leaves increases but adsorption density decreases. It is important to note that desorptions of Zn(II) is rapid and 96% Zn(II) could be eluted in 30 ml of effluent from column. It is interesting to note that adsorption remains maximum (99%) upto 3rd regeneration cycle and then goes down to 91.6% in the 5th cycle. This behaviour indicates that the adsorbent can be used successfully three times after regeneration for the removal and recovery of Zn(II) from waste water. The removal of Zn(II) was 93.02% when 50 ml of the waste treated with 1.0 g of adsorbent. The adsorbed Zn(II) was then recovered (95.3%) with 0.05M HCl.
Chapter 3 describes the adsorption studies of Ni(II) by fruit peel of orange. The adsorption behaviour of different metal ions on orange fruit peel is in the order: Ni(II) > Cu(II) > Pb(II) > Zn(II) > Cr(VI). The adsorption increases with increasing contact time and the equilibrium is attained after 2 h. Adsorption increases with increase in temperature. Thermodynamic parameters such as standard free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$), and entropy change ($\Delta S^0$) were also calculated. The adsorption data has been analysed in the light of Langmuir and Freundlich adsorption models. The Langmuir isotherm is valid for monolayer adsorption onto the surface of the adsorbent containing finite number of identical sites. The increase in Freundlich constant ($K_f$) values with rise in temperature also confirms that the process is endothermic. The maximum adsorption occurs at pH 6 (97.5%) but adsorption decreases when pH is increased further. The desorption of Ni(II) is rapid and 95.8% Ni(II) could be eluted in 30 ml of effluent from the column. The desorption of Ni(II) from a solution containing 50 mgL$^{-1}$ Ni(II) by batch process was 76%. The adsorbent can be used successfully 4 times after regeneration for the removal and recovery of Ni(II) from wastewater. The adsorbed Ni(II) was recovered (93%) with 0.05M HCl from electroplating wastewater.

Chapter 4 deals with the adsorption studies of Cd(II) using teak leaves (Tectona grandis) as adsorbent. The maximum adsorption (93%) is observed at 20 mgL$^{-1}$ initial Cd(II) concentration and decreases to only 81% when initial concentration is increases to 100 mgL$^{-1}$. The adsorption increases with increasing contact time and the
equilibrium is attained after shaking for 2 h. Adsorption also increases with increase in temperature. Thermodynamic parameters were also calculated. The adsorption of Cd(II) on teak leaves increases when pH of the system is increased from 3 to 8. The adsorption data are described by Langmuir and Freundlich isotherm. The plot of $1/x/m$ vs $1/C_e$ is linear showing the applicability of Langmuir isotherm. The values of Freundlich constant $(K_f)$ are also very high and increase with the increase in temperature indicating that Cd(II) ions are strongly adsorbed and adsorption process is endothermic. The adsorption of Cd(II) decreases with increase in particle size and peak value was observed by the finest particle probably because of the large surface area. The desorption of Cd(II) is rapid and maximum Cd(II) is recovered within first fraction (84%) while complete recovery is observed in four fractions (40 ml). However, in batch process, recovery of Cd(II) is slow and incomplete (86%) when desorption was carried out with 50 ml of 0.05 M HCl solution.

Chapter 5 describes the studies of adsorption behaviour of some aromatic amines on pyrolusite and activated carbon and recovery of β-naphthylamine from water sample. Pyrolusite shows remarkable sorption capacity for diphenyl amine (DPAM) and β naphthyl amine (βNAM) as compared to aniline. The adsorption on both the adsorbents followed the order:

\[
\text{Activated Carbon}: \quad \text{DPAM} = \beta \text{NAM} > \alpha \text{NAM} > \text{Aniline} \\
\text{Pyrolusite} : \quad \text{DPAM} = \beta \text{NAM} > \alpha \text{NAM} > \text{Aniline}
\]
The maximum adsorption of β NAM occurred in the concentration range 4-20 μg mL⁻¹ on pyrolusite (95%) and 4-50 μg mL⁻¹ on activated carbon (100%). The effect of various doses of activated carbon on the adsorption of β NAM confirm Langmuir and Freundlich isotherms whereas Freundlich isotherm is obeyed by pyrolusite. The adsorption of β NAM on both the adsorbents is not affected in presence of DPAM over a wide range of their initial concentrations (20-60 μg mL⁻¹). The desorption studies on both the adsorbents were carried out by batch as well as by column operations using various solvents. It was observed that the recovery of β NAM on activated carbon is poor as compared to pyrolusite and excellent results were obtained when a mixture of n-hexane and isopropanol (91:1) was used as eluent.
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Certificate

This is to certify that the work presented in this thesis entitled "Studies on Treatment and Disposal of Industrial Waste" is the original piece of research work of Mr. Rais Ahmad, carried out under my supervision and guidance. The work submitted in this thesis has not been submitted elsewhere for the award of any other degree or Diploma.

RIFAQAT ALI KHAN RAO
Supervisor
Dedicated to My Parent & Teachers
Acknowledgements

In the name of Allah the most benevolent and merciful, I owe a debt of profound gratitude to Dr. Rifaqat Ali Khan Rao, my supervisor, for his scholarly guidance, healthy criticism and keen interest throughout the study.

I express my sense of indebtedness to Prof. Mohammad Ajmal for his outstanding contribution and invaluable assistance to me.

My sincere thanks are also due to Prof. K.G. Varshney, Chairman, Department of Applied Chemistry, A.M.U., Aligarh for providing me all the requisite facilities available in the department.

I wish to present a token of deep appreciation to my seniors Dr. Jameel Ahmad, Dr. Shamim Ahmad and Dr. Shamsul Haq for their constant encouragement, moral support and friendly cooperation during the entire course of research.

I express my heartfelt reverence to my parent whose good wishes and sacred blessings have always been a source of inspiration in accomplishing this task.

(Rais Ahmad)
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CHAPTER 1
CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION:

Today, as never before, planet earth stands in need of mankind's watchful eye over its endangered ecological balance to avert its tragic extinction by population and plunder. The chaotic and shortsighted exploitation of nature has produced a set of conflict situations in the utilization of nature. Many of the situations undoubtedly have their roots deep in human history. Nevertheless, it is only the unprecedented growth of productive forces and their operation in conditions of competition. The absence of planning and the insufficiency of our knowledge of nature which has actually aggravated them and given them a global character. It will be better to express in the words of Naik poem's Threatened survival:

As I walk
Through the lovely green stretch of grass and trees
And, enjoy the freshness of air
I feel sad
For this many not last longer.
There was a time
When man and nature
Were in complete harmony
But now,
Man has become mean and selfish
And can not understand
Nature's agony and anguish
Natural resources are depleting
Wildlife is perishing
And Man is advancing
Advancing at the cost of his own degradation.
Take step now
Or it will be never
And man is going to suffer forever.

The world we live in, if it is to use science and technology must first stress the fundamental values cherished over the ages and the imperative need to preserve and promote them. Here, science is no longer Frankenstein’s monster, but a creative intelligence, which raises humanity in harmonious living to celestial heights. If we misuse science for negative noxiousness or aggressive violence or sensual pleasure we betray the gift granted to us by the supreme power.

The concept of environmental pollution is however, not new (Train, 1976; Rachel, 1960). Even in the thirties Robert Frost described in the poem “New Hampshire” the concern of the “environmentalist” and sounded a note of warning which is quite relevant even today. “How many times it thundered before" ”Franklin" took the hint. How many apples fell on Newton’s head before he took the hint ! Nature is always hinting at us, hint over and over again, and suddenly we take the hint”. Indeed, man has started to look at the problem seriously only after the pollutants and poisons in the air, earth and water piled up to the point where they posed a serious threat to human life. It is only now he is realizing and hence, the feeble call "back to nature" is now gaining momentum.
Millions of tonnes of toxic and objectionable material is daily being disposed off in the environment as a result of industrialization which has led to catastrophic episodes. India is not free from these tragic episodes such as methyl isocynates gas leakage from Union Carbide Factory (Bhopal), killing about three thousand people (1984). Oil slicks due to gulf war and near home when tanker transporting oil ran a ground and more recently arsenic poisoning in lake of W. Bengal have been reported (1999).

A challenging task for the environmental chemist is the removal of these pollutants often found at trace level in various medium of the environment. Today organic as well as inorganic pollutants have perhaps become more important as they are not only toxic but often carcinogenic and affect physiological processes of living things. On the other hand it is very difficult to separate as well as identify the complex organic mixtures. For many years attention has been paid to the development to field method as they have a wider applicability. Conventional method of heavy metal determination in general perform satisfactory. However, recent development in instumentation has made this easier where HPLC (High performance liquid chromatography) is playing an exclusive and notable role as one of the most powerful methods of separation. The excellent examples are the separation of polycyclic aromatic hydrocarbons. Atomic absorption spectrometer, X-ray fluorescence and Inductively coupled plasma mass spectrometry (ICP-MS) are the recent unique tools for inorganic and organic analysis. The most common method for the removal of heavy metals involves hydroxide precipitation.
on the basis of its performance and ease of operation. The other available methods include evaporation, ion exchange, adsorption, electrodialysis, electrolytic extraction, reverse osmosis but many of them are used in special circumstances because of their relatively high cost in separation.

In recent years the adsorption technique for the removal and recovery of heavy metals and organic pollutants from industrial wastes has received a great deal of attention. As the use of adsorbent will not only cut down the costs but also increase its multidirectional application.

1.2 ENVIRONMENTAL POLLUTION:

Pollution of the environment is one of the most horrible ecological crisis to which we are subjected today. We know that three basic amenities for living organism are air, land or soil and water. Sometimes in the past, these amenities were pure, virgin, undisturbed, uncontaminated and basically most hospitable for living organisms, but the situation is just the reverse today because progress in science and technology is also leading to pollution of environment and serious ecological imbalance which in long run may prove disastrous for mankind. Environmental pollution is the result of urban-industrial technological revolution and speedy explosion of every bit of natural resources. The mad rat race among the nation over the entire globe for the development jeopardised the existence of man itself. The craze of progress in agriculture, industry, transportation and technology is taken as the general criterion of development of any nation. Such activities of man
has created adverse effects on all living organism in the biosphere. Rapid industrialization has left with us polluted rivers, contaminated soil, depleted wild life and exhausted natural resources. Today the environment has become foul, contaminated, undesirable and therefore, harmful for the health of living organisms including the man. The term environment, as far as pollution is concerned includes the air, water and noise. Thus pollution is generally defined as "The addition of the constituents to water, air or land, which adversely alter the natural quality of environment".

Today India, which occupies seventh place among the industrialized developing countries of the world, is provided with a good industrial infra-structure in industries like Chemical, Power, Nuclear energy, Food, Petroleum, Pesticides and Plastics. A rapid progress in atomic and nuclear energy has added a huge amount of radioactive in the atmosphere. A number of industrial effluents and emission, especially toxic heavy metal and gases are spread into the water and air daily. Thus, the environment is deteriorated to such an extent that it has crossed the critical limit and has become lethal to all organisms including man.

The environmental pollution is thus the evil of all man made progress. It is only the industrialized countries which are threatened with the deterioration in the environment, but the menace is rapidly growing in India too.

POLLUTANT

It is evident, therefore, that every human society, be it rural, urban, industrial or most technological and scientifically advanced.
disposed off certain kinds of waste products as well as by-products which injected into the environment in so large quantities that they affects the normal functioning of the ecosystem are collectively known as pollutant which have adverse effect on plants, animals and human beings.

Some of the most important and common pollutant of developed and developing countries are deposited matter (sulphur dioxide, fluorine, ozone, ammonia etc.), chemical compounds (aldehyde, detergents, hydrogen fluoride, arsenes, phosgene etc.), toxic metals (cadmium, mercury, nickel, lead, zinc, iron etc.), economic poisons (herbicides, pesticides, fungicides, insecticides, rodenticides etc.), fertilizers (N, K, P), sewage (human waste), radioactive substances (argon-41, cobalt-60, caesium-137, iodine-131, krypton-85, astronium-90, tritium and plutonium-239), noise and heat.

Classification of pollutants:

Pollutant can be classified in a number of ways: for example

(a) On the basis of their forms in which they exist in the environment after their release. On this basis they can be classified as primary and secondary pollutants.

(1) Primary Pollutants:

Substances emitted directly from an identifiable source. These pollutants exist as such after being added or released into the environment. Examples are sulphur dioxide, nitrogen oxides etc.
(2) Secondary Pollutants:

Substances derived from primary pollutants by chemical reactions. For example, primary pollutant such as hydrocarbons and nitrogen oxides present in the environment, react in presence of sunlight to form a group of nitrous compounds like peroxyacyl nitrate (PAN) which is a secondary pollutant.

(b) From ecosystem point of view, pollutants may be classified as biodegradable and non-biodegradable.

(1) Biodegradable Pollutants:

These include particularly domestic sewage. If organic wastes drain out from residential area are easily degraded by micro organism, then they become useful for various purposes in the ecosystem. The domestic sewage can be readily decomposed by natural processes or by engineered systems (such as municipal sewage treatment plant) which enhance capacity of the nature to decompose and recycle. However, if these pollutants enter the environment in such a large quantities that complete degradation may not be possible then they become hazardous for the environment.

(2) Non-biodegradable Pollutant:

These include pollutants from various sources such as aluminium, iron, mercury salt, phenolic compounds and DDT which either not degrade or degrade very slowly or partially thereby polluting the environment. Such pollutants are harmful even in low concentration. These
pollutants not only accumulates but are often biologically magnified as they move in biochemical cycles along food chains. They may also react with other compounds present in the environment to produce even more toxic additional products. Their high concentration may even more fatal. These pollutants decrease the rate of photosynthesis by affecting the planktons, thus, disrupting the natural balance existing between oxygen and carbon dioxide.

**Classification of Environmental Pollution:**

1. **Water**
2. **Air**
3. **Soil or land**

**1. Water Pollution:**

Water pollution may be defined in a number of ways:

(i) Alteration in physical, chemical and biological characteristic of water which may cause harmful affect on human and aquatic biota. (Restoring the Quality of our Environment, Report 1965, President Science Advisory Committee, Washington, USA).

(ii) The deterioration in physical, chemical and biological properties of water brought about mainly by human activities and natural resources. (C.S. Southwick 1976, Ecology and the Quality of Our Environment, New York).

(iii) Foreign substances, either from natural or anthropogenic sources contaminating water supplies may be harmful to life because of
their toxicity, reduction of normal oxygen level of water, aesthetically unsuitable and spread epidemic diseases (World Health Organization, 1966).

(iv) The presence of any toxic substance in water that degrades the quality to constitute health hazards or impair its usefulness. (United States Public Health Service).

Thus, water pollution disturb the normal use of water for irrigation, agriculture, industries, public water supply and aquatic life. It is now considered not only in terms of public health, but also in terms of concentration, aesthetics and preservation of natural beauty and resources. Actually it represents the state of deviation from the pure condition, where-by its normal function and properties are affected. Any shift in naturally dynamic equilibrium existing among environmental segments i.e hydrosphere, lithosphere or sediments give rise to the state of water pollution. Water pollution is mainly caused by:

(a) Natural processes in which the decomposed vegetable, animal and weatherd products are brought into main water resources. All these processes are independent on each other and lead to deterioration of natural environment. For instance, if organic waste is added to water, it will not only influence the chemical characteristics, but will also effect color, odour and biological properties of water.

(b) Anthropogenic processes includes industrial, agricultural, urban, domestic, radioactive, mining sources, use of pesticides and fertilizer by man. These pollutants are constantly poured in water,
deteriorating it to such an extent that it becomes unfit for living communities.

**Types of Water Pollution:**

Water pollution can be classified mainly into three categories:

(a) Physical pollution of water
(b) Chemical pollution of water
(c) Biological pollution of water

**a) Physical Pollution:**

Many industrial wastes, which are discharged into the water bodies have a pronounced color. In most cases the color is due to organic dyes, but there are some highly colored substances of minerals origin e.g. compounds of iron and chromium. When two different trade wastes interact in a stream or when a trade effluent and substances present naturally in a stream interact, an intense coloration is produced. An example of this is the reaction between mine and the natural bicarbonates alkalinity of a river to give an unsightly reddish brown opalescence. Moreover, a physical characteristic of sewage and of most industrial wastewater is their turbidity, which is caused by the presence of very finely divided suspended matter or colloidal matter. Apart from that the heated trade effluent from factories, mills and the large volumes of warm, cooling water from electricity generating stations, which are discharged into the rivers or canals may easily cause a temperature rise of several degrees. This can cause deleterious effects on the flora and fauna of the stream.
(b) Chemical Pollution:

(i) Organic Pollution: This kind of pollution is due to the presence of proteins, fats, carbohydrates and other organic substances found in sewage and trade wastes. Household waste in sewage and faecal matter are the principal contributors of carbohydrates and proteins in water. The main components of protein deteriorating water bodies consist of aminoacids, albumin, gelatin, casein and keratin. These compounds undergo putrefaction by bacterial action to release sulphur and phosphorus compounds producing particularly gases like hydrogen sulphide and sulphur dioxide which in turn cause putrid and musty smell in water. Oil are the potential pollutants originating from petroleum drilling. The presence of oil in water course is undesirable since it creates aesthetic problems. It easily spread over the water surface inhibiting diffusion of oxygen and reaeration of water. Oil thickness up to 0.001 millimeter creates a marked effect on the absorption of oxygen in water. The presence of acetaldehyde, furfural, formaldehyde and vanillin etc. cause odour in water, inhibit algal growth and are toxic to fish and other aquatic animals. Polychlorinated biphenyls (PCB) used in dielectrics, lubricants and plasticizers, cause several physiological disturbances in man. In animals, PCBs affect the central nervous system and respiratory tract.

Phenolic compound enter into the water system mainly through trade wastes. They produce bitter taste, when present in low concentration in water while their higher levels result in pain, renal irritation, severe shock and possibly death. Several polynuclear aromatic hydrocarbons are
observed in water bodies creating carcinogenic effects on man and animals. Benzene like compounds cause odour pollution in water.

(ii) Inorganic Pollution:

Many industrial wastes contain corrosive inorganic acids or alkalies which can damage a stream by breaking down its natural buffer systems and altering its normal pH value. Ammonia, free chlorine, hydrogen sulfide and salts of many heavy metals (copper, zinc, lead, nickel and chromium etc.) are the toxic inorganic substances (Table 11). Any appreciable amounts of these compounds may present or inhibit self purification of rivers and may prove toxic to fish and other aquatic life. The concentration of copper sulfate that will kill trout, perch and black bass are 0.14, 0.75 and 2.1 ppm respectively (Luis Klein, 1957).

(c) Biological Pollution:

Biological pollution is often a secondary result of pollution by sewage. It consists of pathogenic bacteria, certain fungi, algae, viruses, photogenic protozoa, parasitic worms and plants or animals which for some reason either multiply excessively in a stream or are otherwise undesirable, harmful or injurious.

The most widespread form of biological pollution is the contamination of water by pathogenic bacteria derived from sewage.
### Table 1.1 Toxic trace elements in natural waters and wastewater

(De, 1989)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sources</th>
<th>Effects and significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Mining by-products, pesticides, chemical waste.</td>
<td>Toxic possibly carcinogenic</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Industrial discharge, mining waste, metal plating, water pipes</td>
<td>Replaces zinc bio-chemically, causes high blood pressure, kidney damage, destruction of testicular tissue and red blood cells, toxicity to aquatic biota</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Coal, nuclear power and space industries</td>
<td>Acute and chronic toxicity, possibly carcinogenic</td>
</tr>
<tr>
<td>Boron</td>
<td>Coal, detergent formation, industrial waste.</td>
<td>Toxic to some plants</td>
</tr>
<tr>
<td>Chromium</td>
<td>Metal plating, cooling tower water additive, (chromate) normally found as Cr(VI)</td>
<td>Essential trace element, possibly carcinogenic as Cr(VI)</td>
</tr>
<tr>
<td>Copper</td>
<td>Metal plating, industrial and domestic waste, mining, mineral leaching</td>
<td>Essential trace element not very toxic to animals, toxic to plants and algae at moderate levels.</td>
</tr>
<tr>
<td>Fluorine</td>
<td>Natural geological sources, industrial waste, water additive</td>
<td>Prevents tooth decay at about 1 mgL⁻¹ causes mottled teeth and bone damage at about 5 mgL⁻¹.</td>
</tr>
<tr>
<td>Lead</td>
<td>Industry, mining, plumbing, coal, gasoline</td>
<td>Toxic causes anemia, kidney disease, nervous disorder, destruction of wildlife.</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mining industrial waste, acid mine drainage, microbial action on manganese minerals at low pH</td>
<td>Relatively non-toxic to animals toxic to plants at higher levels.</td>
</tr>
</tbody>
</table>
Mercury | Industrial wastes, mining pesticides, coal | Highly toxic to animals as well as plants
Molybdenum | Industrial waste, natural sources | Possibly toxic to animals but essential for plants
Selenium | Natural geological sources, sulphur | Essential at low levels but toxic at higher levels
Zinc | Industrial waste, metal, plating, plumbing | Essential in many metalloenzymes, toxic to plants at higher levels

2. Air Pollution:

The addition of any substance that will alter to some degree the physical and chemical properties of clean air. Such a substance could be considered as an air pollutant.

The five major types of substances known as primary pollutants which account for more than 90% of the air pollution problems are:

i) Carbon monoxide (CO)
ii) Nitrogen oxides (NOx)
iii) Sulphur oxides (SOx)
iv) Particulates

The air pollution originates from processes such as evaporation, chemical and nuclear reactions resulting in the release of high concentration of the contaminants into the atmosphere. The gaseous wastes from automobiles exhaust and factories, chimneys as well as primitive forms of heating (e.g. burning coals and cowdung cakes) are the major sources of air pollution (Copper and Rossano, 1974; Baner
The present average composition of clean dry air is represented in Table 1.2.

**Table 1.2 : Concentration of Gases Comprising Normal Dry Air**  
*(Stern, 1968)*

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentrations (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>780900</td>
</tr>
<tr>
<td>Oxygen</td>
<td>209400</td>
</tr>
<tr>
<td>Argon</td>
<td>9000</td>
</tr>
<tr>
<td>CO₂</td>
<td>315</td>
</tr>
<tr>
<td>Neon</td>
<td>18</td>
</tr>
<tr>
<td>Helium</td>
<td>5.2</td>
</tr>
<tr>
<td>Methane</td>
<td>1.0 - 1.2</td>
</tr>
<tr>
<td>Krypton</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.5</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.08</td>
</tr>
<tr>
<td>Nitrogen Oxide</td>
<td>0.02</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.01 - 0.04</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3. **Soil Pollution**:

The problem of maintenance of the fertility of soil is also important as agricultural lands represents the most important permanent national asset for a country like India. It is for this reason that the question of any deterioration of soils likely to result from sewage or industrial waste irrigation should receive the most important consideration.
The harmful effects or infertility of sewage or industrial waste irrigated soil is due to any one or a combination of the following factors:

(a) Difficulty of carrying out agricultural operations.
(b) Anaerobic conditions in soil.
(c) Restriction of root zone of plants.
(d) Smothering of the crops by the flora of waterlogged lands.
(e) Possibility of a high concentration of salts particularly sodium salts.

Salts may retard adsorption of nutrients and water or may themselves be toxic or lead to alkaline conditions. Anaerobic conditions also retard the bacteriological activity, which is essential for nitrification.

1.3 HEAVY METAL POLLUTION:

Heavy metals are those elements having a density more than 5 times that of water. They are usually present in trace amounts in natural waters and many of them are toxic even at very low concentrations. The problem arising from toxic metal pollution of the environment due to the increasing use of a wide variety of heavy metals in industry and in our daily life, have assumed serious dimensions.

Enhanced levels of heavy metals in aquatic environment are of great concern because of:

i) Possibility of accumulation of these metals in human body and building up with time to toxic levels.

ii) Bio-concentration/accumulation and magnification by aquatic organisms.
iii) Chronic and sub-lethal effects to organisms at low concentrations.

iv) Possible intake through drinking water and aquatic food.

v) Carcinogenic and teratogenic possibilities of some heavy metals and their compounds.

vi) Phyto-toxicity of heavy metals.

vii) High sensitivity of children towards some of the heavy metals.

viii) Synergistic effect of heavy metals to organisms.

ix) Persistence in the environment with possibilities for environment transformation into more toxic compounds.

It is a matter of grave concern that an increasing quantity of heavy metals are being discharged in our resources, especially since a large number of industries discharge their metal containing effluents to fresh water without adequate treatment.

The information on metal toxicity to human beings is derived mostly from health surveys among workers engaged in mining and processing of these metals. Environmental degradation is mostly due to metals like Pb(II), Cd(II), Hg(II), Ni(II), Cu(II), Cr(VI) and Cr(III) which have been the source of major concern.

Lead is a toxic element and it accumulates in the body, mainly in the bones. It is also found to accumulate in brain, kidney and muscles. Lead poisoning is not due to occasional exposure to small doses but due to permanent cumulative effects. However, death may result in extreme cases of lead poisoning. Due to discharge of industrial waste waters
such as printing, dyeing and oil refineries etc. its concentrations in water increases. Cadmium accumulates in various parts of the body (liver, pancreas, kidney etc.) and causes the painful bone diseases itai-itai. Electroplating, chemical industries, milling and mining effluents are the major sources of cadmium. Mercury is also a highly poisoning substance and is mainly toxic in the form of methyl mercury. It affects the central nervous system and may be fatal at higher doses. Copper in the natural waters also results in higher concentration due to pollution. It is used as a pesticides with sulphate and also as an algicides separately. Although it passes as such through the body but there is evidence of accumulation in liver in trace quantities. Apart from these metals, there are certain reports of chromium accumulation at higher concentrations irrespective of their valency. Hexavalent chromium is found to be more toxic. It causes cancer in respiratory tract, when inhaled in large quantities occupationally. However, there is no evidence of cancer due to chromium intake through diet or ambient water (National Academy of Science, 1974). It results in higher concentration in the wastes from electroplating, paints, dyes, chrome tanning, explosives, ceramics and paper industries etc. (Trivedy and Goel, 1975).

1.4 SOURCES OF HEAVY METAL POLLUTION

The heightened awareness of the deleterious effects of heavy metal pollution of the environment have posed a serious threat. The problem arising due to the increasing use of a wide variety of heavy metals in industry and in our daily life however, have assumed serious dimensions. In general, it is possible to distinguish between different
sources from which metal pollution of the environment originates. The sources are:

i) Geological Weathering:

This is the source of baseline or background levels, such as the metals occurring in elevated levels in the water and sediments in areas characterised by metal bearing formations. Obviously mineralised zones, when economically viable are exploited to retrieve and process the ore. This in turn leads to disposal of tailings, discharge of effluents and possibly smelting operations which result in atmospheric pollution of various metals.

Arsenic rich hot springs arising from geothermal activity feed the Waikato River of North Island, New Zealand. Submerged aquatic plants from this river were found to contain a maximum of 650 mg/kg dry mass.

Similarly geothermal sources in North Island are a natural source for mercury enrichment.

ii) Mining Effluents:

The serious effects of mine effluents on the water quality in rivers and lakes, as well as on the biotopes, particularly on the fish population, have been known for many years. One of the very first descriptions of this problem is the fifth report of the 1868 River Pollution Commission (Anon, 1968) in Britain, where especially grave damage was caused by the disposal of toxic metals from lead, zinc and arsenic mines in mid-Wales (Lewin et al., 1977).
(iii) Industrial Effluents:

A large number of industrial effluents contribute to heavy metal pollution of the aquatic environment. The classic example is the discharge of the catalyst methylated mercury chloride into Minamata Bay from a factory manufacturing plastics.

Most of the heavy metals are employed on widely diversified fields, such as in petroleum refining, steel and fertilizer production etc. Apart from the several industries function on the basis where only one specific heavy metal is used for example, chromium in the tanning industry.

Chemical and electrochemical methods are employed in the metal finishing and allied industries for the purpose of protection and/or the decoration of a variety of metal surfaces (Lowe, 1970). Most of the processes are followed by rinsing operations to remove the excess chemicals and other waste material from the treated surface, thus giving rise to effluents containing metals. Notably, pickling and electroplating give rise to high waste metal concentrations. Obviously, most effluent from pickling and dipping operations are strongly acidic and contain appreciable amount of dissolved metals. It has been estimated that the Dow Chemical chlor-alkali plant at Sarnia had discharged 91,000 kg of mercury compounds into the St. Clair River system during the period 1949 to 1972 (Wood, 1972). Polish tannery wastes from chrome tanneries have been reported to vary between 9-14 mgL⁻¹ of chromium (Koziorowski, 1972). Apart from the metal bearing industrial discharges
discussed Table 1.3 reveals that the laundries, ice cream and soft drink manufactures also discharge wastes containing appreciable amount of heavy metals like Cu, Cr, Ni, Zn and Cd.

The textile dyeing and laundry wastes have high chromium contents. The backery wastewater contain high levels of nickel and the fur dresser and dyers discharges exceptionally high concentration of Cu, Cr, Ni, Zn and Cd (Klein et al., 1974).

Wastes from metal finishing operations particularly those from electroplating are among the most toxic of industrial effluents. Since they contain such poisonous constituents as acids, heavy metals viz., Cr, Ni, Cd, Zn and Cu and cyanides. Electroplating waste is one of the major contributors to heavy metal pollution in surface waters (Forstner and Wittman, 1981; Music 1986; Golomb, 1972; Dean et al. 1972). For this reason electroplating wastes should not be discharged into the surface streams unless extensive dilution is made and they should not be permitted to municipal sewers. Pretreatment of metal finishing wastes at the source, to reduce the concentrations of the toxicants below environmentally acceptable levels can be provided to prepare them for discharge into stream or municipal sewage.

Discharge of dye-bearing wastewater into natural streams from textile, pulp and paper, carpet and printing industries impart toxicity and impedes light penetration. Presence of carcinogens have been reported in the combined wastewater of dyeing and printing units of Udaipur, India (Document on Textile Industries, 1983).
Table 1.3. Metals in Industrial Wastewaters (Kelien et al., 1974)

<table>
<thead>
<tr>
<th>Industry</th>
<th>Average concentration in $\mu$gL$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Meat processing</td>
<td>150</td>
</tr>
<tr>
<td>Fat rendering</td>
<td>220</td>
</tr>
<tr>
<td>Fish processing</td>
<td>240</td>
</tr>
<tr>
<td>Bakery</td>
<td>150</td>
</tr>
<tr>
<td>Miscellaneous foods</td>
<td>350</td>
</tr>
<tr>
<td>Soft drinks and flavourings</td>
<td>2040</td>
</tr>
<tr>
<td>Ice cream</td>
<td>2700</td>
</tr>
<tr>
<td>Textile dyeing</td>
<td>37</td>
</tr>
<tr>
<td>Fur dressing and dyeing</td>
<td>7040</td>
</tr>
<tr>
<td>Miscellaneous chemicals</td>
<td>160</td>
</tr>
<tr>
<td>Laundry</td>
<td>1700</td>
</tr>
<tr>
<td>Car wash</td>
<td>180</td>
</tr>
</tbody>
</table>

(iv) Domestic Effluents:

The domestic waste water constitute the largest single source of elevated metal concentration in rivers and lakes. Solid waste particles may cause metal enrichment of the suspended load in the waters. The concentration of copper, lead, zinc, cadmium and silver reveal a marked influence of domestic effluents in the receiving waters (Preuss and Kollmann, 1974).
The use of detergents also creates a possible pollution hazard, since common household detergent products can affect the water quality. Many enzyme detergents contain traces of elements like Fe, Mn, Cr, Ni, Co, Zn, Sr and Ba (Angino et al., 1970).

v) Urban Storm Water Run Off:

The urban storm water runoff presents a serious problem of heavy metal contamination. Heavy rainfall in urban area is no longer regarded as only a downpour of "rain water" since they often contain shock loads of metal contaminants (Sartor et al., 1974). A statistical summary revealed that urban storm water runoff has long been recognized as a major source of pollutants to surface waters (Bradford, 1977).

The contamination, however, occurs during period of storm runoff, whereby trace elements results from atmospheric emissions and are subsequently deposited on various surface material to the nearby drainage system. After monitoring heavy metals from two heavily urbanized watershed at Lodi, New Jersey, Whipple and Hunter (1977) detected high concentration of lead, zinc and copper after a storm event.

vi) Atmospheric Sources:

Natural and man made processes have resulted in metal containing air-born particulate. Depending on prevailing climatic conditions, these particulate may become wind-blown over a great distances, nonetheless they are subjected to the fate that they are ultimately returned to the Lithosphere as precipitation by rain or snowfall.
A study conducted by Shiomi (1973) has revealed that 15-36% of the Pb entering Lake Ontario from the Niagara River was attributable to atmosphere precipitations.

1.5 SURVEY OF LITERATURE

1.5.1 Treatment Technology for the removal and recovery of heavy metals and organic compounds from industrial wastewater:

The presence of heavy metals in the environment can be detrimental to a variety of living species. Therefore, the elimination of heavy metals from water and wastewater is important in order to safeguard public health. Several methods have been proposed for the removal and recovery of heavy metals such as:

(i) Precipitation:

Ions of the heavy metals occur in wastes from the metal finishing industries and in several other types of industrial wastes. These metal salts are usually accompanied by acids that can be destroyed by neutralization. If the neutralizing agent is strong enough and if a sufficient quantity is employed, the pH can be carried beyond the neutral point of 7; at a pH of 8 or 9; most of the heavy metals are precipitated as hydroxides or basic salts. However, lime is preferred over the more expensive sodium or potassium hydroxide.

Cupric oxide forms from the hydroxide (Stumm and Morgan, 1970) has minimal solubility between pH 9.0 and 10.3. A minimal solubility of 0.01 mgL⁻¹ has been reported in the above pH range from laboratory studies (Jenkins et al., 1964). This value corresponds closely
to the theoretical minimum effluent level which could be achieved by precipitation.

Maruyama et al. (1972) studied the removal of copper from municipal wastewater enriched up to 5.0 mgL$^{-1}$. Various combinations of lime and ferrous sulfate addition were examined for the treatment effectiveness. After chemical addition, flocculation and settling, the effluent was sand filtered and passed through activated carbon columns. Best copper removal was achieved at pH 6.0 with the addition of ferrous sulfate only. Similar improved treatment has been reported for alum flocculation at pH 6.8-7.0 which reflects the phenomenon of coprecipitation (Culp and Culp, 1974).

A significant problem in achieving low residual copper concentration is the presence of complexing agents notably cyanide and ammonia. Therefore, copper treatment may depend strongly on the removal of complexing agents. One method of avoiding cyanide treatment is to use the pyrophosphate copper plating process (Crowle, 1971). Conventional lime treatment of pyrophosphate is not effective since the bath is already at pH 8.3-8.8. Elevation of pH to 12.0 with lime which precipitate calcium pyrophosphate and thus allow simultaneous precipitation of copper hydroxide (Parsons and Rudolfs, 1951).

Treatment of cupric wastewater with hydrazine or some other reducing agent and sodium hydroxide reduces copper to cuprous form and such a system may be operated at pH 7-8 (Volco and Copper, 1971: Pinner and Crowle, 1971).
Limited information is available on sulfide precipitation of copper (Rosehart and Lee, 1972; Larsen et al., 1973). Copper was reduced from 20 mgL\(^{-1}\) to below detectable limits by sulfide precipitation from a gold ore extraction wastewater. Treatment by coprecipitation with alum yielded equivalent results (Cotton and Wilkinson, 1962). In field studies on an acid mine drainage waste, the waste was first lime neutralized to pH 5.0 to precipitate iron and aluminium and then with barium sulphide for removal of other heavy metals. Copper was reduced from initial levels of 50-115 mgL\(^{-1}\) to below 0.5 treated at pH 6.5 mgL\(^{-1}\) (Weiner, 1967).

Cadmium forms an insoluble and highly stable hydroxide at alkaline pH (Cotton and Wilkinson, 1962). Most effective cadmium hydroxide precipitation occurs between pH 9.5 and 12.5. Freshly precipitated cadmium hydroxide has been reported to leave approximately 1.0 mgL\(^{-1}\) of residual cadmium in solution at pH 8, but this is reduced to 0.1 mgL\(^{-1}\) at pH 10 (Jenkins et al., 1964). Precipitation at pH above 11 has been reported to yield an effluent containing cadmium level of 0.00075 mgL\(^{-1}\). Sand filtration slightly reduced this residual cadmium concentration to 0.00070 mgL\(^{-1}\) (Culp and Culp, 1974). It has been shown that co-precipitation with iron hydroxide at pH 8.5 improves cadmium removal (Anderson et al., 1971; Weiner, 1967) and that co-precipitation with aluminium hydroxide is also effective for cadmium, as well as zinc and nickel (Culp and Culp, 1974).

An evidence for the beneficial treatment effect of cadmium by co-precipitation with iron hydroxide has been studied by Maruyama et al. (1972).
In hydroxide precipitation of cadmium from a waste stream at a machine plant, an effluent of pH 9.0 and cadmium concentration of 0.54 mgL\(^{-1}\) was reported for the lime precipitation process (Hansen and Zabban, 1959).

An effective cadmium removal had been achieved in a pilot plant lime coagulation - settling process. The process achieved 94.5% cadmium removal from the trace quantities present (Linstedt et al., 1971).

In the presence of complexing agents (e.g. cyanide), it is difficult to precipitate cadmium ion (Weiner, 1967). Therefore, effective precipitation of cadmium is dependent upon prior cyanide removal. Chalmers (1970) reported treated effluents containing cadmium concentration of 0.7 mgL\(^{-1}\) after cyanide chromium treatment plus neutralization and sand filtration.

A proprietary hydrogen peroxide oxidation precipitation system has been developed which simultaneously oxidizes cyanides and precipitates the oxide of cadmium.

The hydroxide precipitation with lime may be unsatisfactory for cadmium, due to the high pH required for effective treatment (Dean et al., 1972). The use of sulfide for cadmium precipitation appears feasible, although it has had only limited application (Larsen et al., 1973; Shimoiizaka 1972).

Trivalent chromium can be removed as insoluble chromic hydroxide Cr(OH)\(_3\) by precipitation with caustic soda or lime.
(Besselievre, 1969). The precipitation process is most effective at pH 8.5-9.5 due to the low solubility of chromic hydroxide in this range.

Soda ash has been used to precipitate trivalent chromium (Besselievre, 1969) although the most commonly employed chemical for precipitation is lime. The chromium content of electroplating waste was reduced from 140 to 1.0 mgL\(^{-1}\) by neutralization and precipitation with lime at pH 7-8 (Avrutskii, 1969). A coagulant aid was employed to improve the chromic hydroxide precipitate removal (Connor et al., 1962).

Chromate reduction have been achieved by sodium metabisulfite to below 0.1 mgL\(^{-1}\) followed by neutralization of the waste with lime to pH 9.0. Precipitation of chromic and other metallic hydroxide, and setting (Werner, 1972) has been found to be a promising technique. Trivalent chromium levels below 0.2 mgL\(^{-1}\) can be achieved by such treatment (Curry, 1972).

Sedimentation of the precipitate was improved by addition of an anionic polyelectrolyte. Plant effluent was reported to contain no hexavalent chromium and average 0.75 mgL\(^{-1}\) trivalent chromium (Anderson and Iobst, 1968).

(ii) Reduction:

In reduction treatment technique, the pH of the waste water has to be lowered with sulphuric acid and convert the hexavalent chromium to trivalent chromium with a chemical reducing agent such as sulfur dioxide, sodium bisulfite, metabisulfite or ferrous sulfate. The trivalent
chromium is then removed, usually by precipitation with lime (MacDougall, 1954; Besselivere, 1969).

Sulfur dioxide is the most popular reducing agent in treatment of chromium containing wastes, primarily because it is relatively cheap (Stone, 1972). Its use to treat chromium in metal finishing wastes at a Boeing plant has been reported (Halse et al., 1960). The pH of the waste was adjusted to 2.5 by adding sulfuric acid before reduction. Sulfur dioxide, used to treat chromic acid plating bath and chromic acid bath wastes yielded less than 1.0 mgL⁻¹ residual hexavalent chromium (Shink, 1968).

An unusual source of sulfur dioxide, washed out of the power house stock gas was used as the chemical reducing agent for converting Cr(VI) to Cr(III). Sodium bisulfite is employed as a supplement (Lacy and Cywin, 1968) where additional reduction is needed.

In the treatment of electroplating waste containing 140 mgL⁻¹ of hexavalent chromium, reduction was carried out at pH 2.5-2.8, employing sodium bisulfite as the reducing agent (Avrutskii, 1969). The process was reported to reduce hexavalent chromium to the concentration of 0.7-1.0 mgL⁻¹. The replacement of sulfur dioxide with sodium metabisulfite as a reductant has been reported due to industrial health problems associated with gas leakage (Kelsy and Seeds, 1972).

A two-stage chromate reduction process has been utilized for chromium plating rinse water. The use of sodium bisulfite followed by
hydrazine plus soda ash reduced the chromium concentration from 8-20.5 mgL⁻¹ to less than 0.1 mgL⁻¹ in the effluent (Martin, 1973). The use of metabisulfite as a reducing agent for treatment of chromate waste from a metal plating operation (Landy, 1971; Werner, 1972) and sodium hydrosulfite (Martin, 1973) have also been reported.

Several reports also describe the use of ferrous sulfate as a reducing agent for chromate containing wastes. Ferrous sulfate has been found to have the advantage of effectiveness independent of pH (Germain et al., 1968). However, Bennett (1972) claims that ferrous reduction at pH 2-3 proceeds within 30 minutes to a residual hexavalent chromium level to 1.0 mgL⁻¹. In addition, the use of ferrous sulfate to treat chromate wastes containing cyanide results in the formation of very stable ferrocyanide complex which prevents subsequent effective cyanide treatment.

(iii) Ion Exchange:

Ion exchange is capable of achieving very high levels of copper removal particularly from low concentration wastes. Copper removal by ion exchange from 1.02 mgL⁻¹ to less than 0.03 mgL⁻¹ has been reported (Botham and Bryson, 1953). When compared to other treatment methods, for cases where metal recovery is not feasible, ion exchange does not appear to be practicable as it is a costly process.

Treatment of copper rinse solutions containing high ammonia contents has been reported by a selective ion exchange resin. Copper was reduced from 45 mgL⁻¹ to undetectable levels by this process.
Schore (1972) reported that ion exchange reclamation of copper from pickle liquor allowed electrolytic copper recovery and regenerated the acid pickle solution.

There are many ion exchange resins with specificity for cadmium (Mattock, 1968). However, ion exchange method is unsuitable for the recovery of cadmium from mixed cadmium cyanide solution (Oldan and Hesler, 1956).

Relatively little information is available in literature on ion exchange treatment of trivalent chromium. In most of the industrial wastes chromium exists in the hexavalent form and if recovery is preferred, direct ion exchange treatment of the chromate or dichromate is carried out. Different resins are employed to recover each form of chromium (Ross, 1968; Thomson and Miller, 1971).

In the ion exchange system, pH is a critical factor (Anderson, 1974; Calmon, 1974). With proper pH adjustment (4.5-5), chromate was removed from cooling water system even in the presence of high concentration of sulfate and chloride ions. Successful ion exchange treatment of a metal finishing waste has been reported to meet a chromate effluent swtandard of 0.05 mgL$^{-1}$ (Rothstein, 1958). This chromate level is equivalent to a Cr(VI) concentration of 0.03 mgL$^{-1}$.

(iv) Evaporative Recovery:

Use of evaporative recovery has been practiced for over 20 years (Culotta and Swanton, 1970). Recovery of copper by this method
is often more economical than some other metals such as zinc due to its higher cost (Culotta and Swanton, 1971).

In evaporative recovery of chromic acid, all constituents of the wastewater are retained in the concentrated product. In practice, this has been a major disadvantage of evaporative recovery since the build up of impurities often results in defective plating (Pinner, 1973). Plating waste rinse water containing only a few mgL\(^{-1}\) of chromic acid can be concentrated to above 900 mgL\(^{-1}\) (Culotta and Swanton, 1969).

(v) Electrochemical Reduction:

A recently developed process with significant potential application for both concentrated and dilute copper containing wastewater is 'cementation' (Jester and Taylor, 1973; Case, 1974). The process involves percolating the copper wastewater through a bed scrap iron. By oxidation-reduction reaction, copper is cemented onto the iron, with sacrificial iron going into solution.

Reduction of Cr(VI) to Cr(III) has also been successfully applied in an electrochemical treatment process. The hexavalent chromium reacts with both elemental and ferrous iron and gets reduced to trivalent chromium. The reaction has been found to be pH dependent. Complete reduction of a 100 mgL\(^{-1}\) Cr(VI) solution has been reported within 8 minutes, at pH 2.0 (Case, 1974).

(vi) Miscellaneous Processes:

The processes include Reverse Osmosis, Electrodialysis, Freeze and Electrolytic Recovery of metals from different wastes.
Successful pilot scale reverse osmosis treatment (99% rejection) has been reported for copper pyrophosphate and copper cyanide plating bath rinse water. However, available membranes are suitable only over a pH range of 3.5-12.0 (Donnelly et al., 1974). The removal of cadmium from cadmium plating rinse wastes has been reported to the extent of 78 to 99% (Mattock, 1968). A highly selectivity cellulose acetate membrane yielded 92.6% rejection at pH 2.6 and 98.6% rejection at pH 7.6 (Cruver, 1973) for hexavalent chromium containing wastes.

Bovet (1970) has claimed that electrodialysis is economically feasible for treatment of process solutions and rinse waters from plating and metal finishing operations, and for treatment of acid mine drainage, containing heavy metals.

Freeze recovery has also been considered and reported effective as well as economical followed by either reuse or precipitative treatment of the concentrated slurry (Donnelly et al., 1974). About 99.6% reduction of cadmium, to a final concentration of 0.4 mgL\(^{-1}\) (Campbell and Emmerman, 1972) has been achieved by this process.

Direct electrolytic recovery of copper metal is possible from relatively concentrated waste solutions. The electrolytic process generally requires a preconcentration step such as ion-exchange or evaporation. Acid leach solution from copper ore can be electrolysed directly in one application to recover copper (Simpson and Thompson, 1950). Recovery of copper from copper pickling baths presents no
problem but brass pickle solution may cause problems due to the sludges formation (Jackson, 1972).

A new process has been reported (Silman 1971) for the electrolytic treatment of dilute copper cyanide solution. The process consists of a fluidized semi-conducting carbon bed across which a potential is developed.

(vii) Adsorption Processes:

The adsorption studies are significant both theoretically and practically as they can be utilized in the detection, determination and treatment of inorganic and organic pollutants. The use of adsorption processes of solid adsorbents has been considerably developed recently, for the removal of pollutants. It has been found to be very useful and successful in many fields such as the purification processes, water treatment processes and analytical methods.

The removal of residual organic compounds from waste water by activated carbon is considered to be the advanced method that has received great attention (Swanson, 1971). However very limited literature is available on the adsorption of specific compounds. The adsorption of phenol, sodium salts of sulphonated organics and pesticides have been reported by (Morris and Weber 1964, 1966). Snoeyink et al. (1969) found that phenol was adsorbed more extensively by a coal base carbon than by a coconut shell carbon. Kipling (1948) reported pH effects on the adsorption of acetic acid and n-butylamine and concluded that only the undissociated species could be adsorbed.
on activated carbon. However removal was not greater than 20% (for acetic acid) and 25% (for n-butylamine). Cheldelin and Williams (1942) obtained Freundlich isotherms for a large number of amino acids, vitamins and related substances. The important factors noted in their work was the presence or absence of aromatic nuclei and the position of polar groups. Coughlin and Ezra (1968) and Coughlin et al. (1968) has reported that the adsorption of phenol and nitrobenzene was reduced when carbon surface oxides is increased.

Fox et al. (1969) reported activated carbon studies on a waste brine stream containing phenol and acetic acid. The carbon was regenerated with sodium hydroxide. Huang and Hardie (1970) used activated carbon in a physicochemical treatment process on a refinery waste. The removals of chemical oxygen demand (COD) and total organic carbon (TOC) were approximately 80 and 90% respectively. Paulson (1970) reported COD, TOC and biochemical oxygen demand (BOD) removals (65-100%) from primary and secondary effluents of ten petroleum refineries. Vanstone (1969, 1970) used activated carbon process for the treatment of various industrial waste waters and it was reported that average removal of COD from one waste stream containing phenol, benzene and organic amino compounds was about 60%. Singh and Misra (1990) has reported removal of phenolic compounds from water using chemically treated saw dust.

Information on some of the effects of functionality, molecular weight, pH, branching solubility and polarity is available for a group of organic compounds, however these parameters for pure compounds
should be useful in predicting results for treatment of specific waste. The prospects of using several low cost materials as adsorbents for the removal of heavy metals and organic pollutants have been investigated extensively in recent years which are summarized in Table 1.4A and 1.4B.

1.6 AIMS AND OBJECTIVES:

The awareness of the deleterious effects of heavy metals and organic pollutants by their improper disposal into surface water has resulted in an intensive efforts aimed at understanding the interaction as such materials in natural aquatic system and their removal from water and wastewater by various treatment processes. The selection of the treatment process in governed by the nature, composition and flow rate of the industrial effluent. The conventional methods like precipitation of heavy metals in general perform satisfactorily to meet direct discharge requirements but for very dilute effluent, precipitation of heavy metals in difficult unless a coagulating agent is used and that results in the formation of bulky and wet sludge, the disposal of which is a problem. Adsorption is one of the best treatment process for controlling pollution specially for dilute effluent. It is rather a polishing technique which may be used after biological wastewater treatment. The activated carbon is the most widely used adsorbent. Its high cost have led to the search for cheaper and economical substitutes. The rate of adsorption and the extent to which a particular metal is adsorbed depends upon a number of factors. One of them is the nature of adsorbent itself and hence there is scope to examine adsorption
properties of various low cost and easily available materials. It is with this view attention has been given to explore the adsorption properties of various economically viable substances like teak leaves (Tekctona grandis), orange fruit peel (Citrus reticulata) and pyrolusite mineral. Attempt have been made for the removal and recovery of heavy metals from water and electroplating waste water. Pyrolusite, a manganese ore has been used for the removal and recovery of various aromatic amines. The following chapters summarize our findings in these directions.
1.5.2.
Table 1.4A  A Selective summery of Recent work Done on Treatment of Water and Wastewater containing heavy metals.

<table>
<thead>
<tr>
<th>Treatment Methodology</th>
<th>Metals removed from water and Wastewater</th>
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<tr>
<td>Chemical treatment</td>
<td>Iron and Copper</td>
<td>&gt;99.9% removal from chelent cleaning wates</td>
<td>McConnell and Hoy 1988</td>
</tr>
<tr>
<td>Adsorption/co-precipitation</td>
<td>Trace elements</td>
<td>Efficient removal of heavy metals was achieved from power plant wastes</td>
<td>Simon, 1988</td>
</tr>
<tr>
<td>Adsorption by glass powder</td>
<td>Bi(III) or Fe(II)</td>
<td>Maximum removal of Bi(III) or Fe(II) was achieved from aqueous solutions containing trace amounts of elements</td>
<td>Artyukhin et al., 1990</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Rare earth metals</td>
<td>Rare earth metals oxides obtained by treating the rare earth metal contg. liquor with Na$_2$S and NaOH precipitates out rare earth metal carbonates after addition of NH$_4$HCO$_3$-NH$_4$Cl mixed precipitant and polyacrylamide.</td>
<td>He et al., 1989</td>
</tr>
<tr>
<td>Adsorption on aluminium oxide</td>
<td>Cd</td>
<td>Maximum removal occurred at pH 7 and at 40°C.</td>
<td>Lo and Leckie, 1989</td>
</tr>
<tr>
<td>Ion exchange (ion exchanger ANBK-35)</td>
<td>Cu$^{2+}$</td>
<td>Effective removal of Cu from solutions (produced by hydraulic acid decomposition of cobalt containing cakes with ion exchanger ANBK-35.</td>
<td>Voldman et al., 1989</td>
</tr>
<tr>
<td>Adsorption on geothite</td>
<td>Cd</td>
<td>Removal efficiency depends upon some particular pH, temperature and concentration.</td>
<td>Johanson, 1990</td>
</tr>
<tr>
<td>Treatment Methodology</td>
<td>Metals removed from water and Wastewater</td>
<td>Remarks</td>
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<tr>
<td>Precipitation</td>
<td>Cd</td>
<td>Cd is precipitated in a bacterial culture medium, Luria-Bertani broth. The pups obtained after addition of 3mM Cd.</td>
<td>Rayner and Sadler, 1990</td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>K and Heavy metals</td>
<td>Efficient removal of potassium and heavy metals by Ti phosphate and their subsequent desorption with HNO₃.</td>
<td>Smirnov et al., 1990</td>
</tr>
<tr>
<td>Adsorption on Lignite</td>
<td>Co</td>
<td>Maximum removal obtained from ammonical ammonium sulfate solutions.</td>
<td>Nathsarman et al., 1989</td>
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<tr>
<td>Adsorption by soils</td>
<td>Cu</td>
<td>Efficient removal was achieved but adsorption is affected in presence of calcium.</td>
<td>Karnaugh et al., 1989</td>
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<tr>
<td>Co-precipitation</td>
<td>Heavy metals</td>
<td>Trace of Ag, Bi, Cd, Cu, Hg, Pb and Zn separated by carrier precipitation with dithiazone from dil. HNO₃ and HCl solutions.</td>
<td>Beinrohr &amp; Hofbauerova, 1989</td>
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<tr>
<td>Adsorption by lignite</td>
<td>Heavy metals</td>
<td>Maximum removal was obtained from waste water</td>
<td>Saleeva and Kdynov, 1989</td>
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<tr>
<td>Cementation</td>
<td>Metals</td>
<td>99% recovery of metals was obtained from dilute solution.</td>
<td>Schmidt, 1989</td>
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<td>Adsorption on Silica gel</td>
<td>Fe</td>
<td>Separation of Fe was accomplished from uranium.</td>
<td>Chen et al., 1989</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Metal ion</td>
<td>The uptake of the metal ion is rapid by some amine intercalates of a tin(IV) hydrogen phosphate monohydrate. The intercalate appeared to be selective for Cu at low conc. in mixed solution.</td>
<td>Hudson et al., 1990</td>
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<tr>
<th>Metals removed from water and Wastewater</th>
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<tr>
<td>Pb</td>
<td>Adsorption on Fly ash</td>
<td>Efficient removal was accomplished from water containing Pb impurity.</td>
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<tr>
<td>Metals</td>
<td>Cementation</td>
<td>Furthermax, maximum recovery of Ag from chloride containing solutions has been achieved.</td>
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<td>Mn</td>
<td>Adsorption on ruthenium</td>
<td>Maximum removal has been demonstrated.</td>
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<tr>
<td>Co</td>
<td>Ion exchange (resins)</td>
<td>Separation and recovery of manganese and cobalt was obtained from Fe&lt;sup&gt;3+&lt;/sup&gt;.</td>
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<td>Hg</td>
<td>Adsorption on Zirconium oxide</td>
<td>Separation from antimony and neodymium in aqueous solution.</td>
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<td>Y, Mo, W</td>
<td>Precipitation</td>
<td>V. Mo, W were selectively recovered from spent petroleum refining catalysts containing Ni, Co and Fe after calcined and treated with stabilized aq. H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; and NH&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;.</td>
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<tr>
<td>Cd &amp; Zn</td>
<td>Adsorption (in saturated soil columns)</td>
<td>The removal of Cd and Zn was higher in a dynamic system, than in a static (batch) system.</td>
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</table>

References:
- Yadava et al., 1989
- Schmidt & Koscher, 1989
- Herbek, 1990
- Rauf et al., 1989
- Zhang & Ma, 1988
- Chan & Lido, 1988
- Balacharya & Vigneswaran., 1990
- Kohler 1990

Heavy Metals:
- Arsenic, cadmium, copper, mercury, lead, zinc, and chromium precipitated from 10-34-1 (nitrogen, phosphorus, potassium) grade fertilizer solution and wet process phosphoric acid upon the addition of organic reagents.
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<th>Treatment Methodology</th>
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<tr>
<td>Adsorption with Corn glutin</td>
<td>Cd &amp; Mg</td>
<td>Efficient removal of Ca and Mg was achieved from solution. Separation of palladium(II) from transition elements was achieved by using an ion exchange salicylaldehyde formaldehyde resin. Adsorption-desorption behaviour of Zn(II) from aqueous solution is influenced by pH and temperature. Rare earth elements [RE(III)] was quant. copptd. with calcium oxalate which had been pptd. from the Ca of a macrocomponent in biol sample by addition of a substoichiometric. The method however, showed high selectivity for RE(III) from other elements. The maximum adsorption from aqueous solution per unit mass of the α-aluminium hydroxide increase with the increase in temperature. Selective separation of Uranium(VI), Thorium(IV) and Iron(III) from the rare earth elements by cheolating ion exchangers and the subsequent elution of U(VI) and Th(IV) from the exchanger with 1-2M(NH₄)₂CO₃ solution.</td>
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<td>Adsorption on Fe(OH)_3</td>
<td>Zn²⁺</td>
<td></td>
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<td>Co-precipitation</td>
<td>Rare earth elements</td>
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<td>Adsorption by α-</td>
<td>Zn</td>
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<td>aluminium hydroxide</td>
<td>Th(IV), U(VI), Fe(III)</td>
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<td>Treatment Methodology</td>
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<td>Adsorption by Lateritic soil</td>
<td>Zn</td>
<td>Adsorption of Zn is affected in the presence of organic ligands.</td>
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<td>Co-precipitation</td>
<td>Toxic metals</td>
<td>Toxic metals were co-precipitated with iron oxide.</td>
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<td>Adsorption on Bituminus Coal</td>
<td>Cr(VI)</td>
<td>Maximum removal was obtained from highly acidic waste water.</td>
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<td>Ion Exchange</td>
<td>AgNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Recovery of silver nitrate was achieved from wastewater.</td>
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<td>Sorption by Chitosan</td>
<td>Cu</td>
<td>Maximum removal occurred with increasing amino content, from shrimp. Besides the recovery of amino acid is also made.</td>
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<td>Precipitation</td>
<td>Metal ions</td>
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<td>Adsorption on synthetic bifunctional interpenetrating polymer networks</td>
<td>Cu &amp; Co</td>
<td>Alk. earth and some bivalent metal ion such as Co&lt;sup&gt;2+&lt;/sup&gt;, Ni&lt;sup&gt;2+&lt;/sup&gt;, Cu&lt;sup&gt;2+&lt;/sup&gt;, Zn&lt;sup&gt;2+&lt;/sup&gt; and Cd&lt;sup&gt;2+&lt;/sup&gt; were precipitated and extracted with bis (disphenyl-phosphiny) methane and perchlorate.</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Uranium</td>
<td>Maximum removal is acheived by ligands complexing metal ions within the network. Co and Cu affinities were quantified from Langmuir isotherm plots.</td>
</tr>
</tbody>
</table>

Solid ion exchangers are most preferred for the recovery of Uranium from in-situ leach liquors of low-grade ores and from wastewater while solvent extn. is used for U-rich solutions.
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<td>Adsorption by hydrous titanium oxide</td>
<td>Cu</td>
<td>Efficient removal was obtained from the aqueous solution.</td>
<td>Chen and Ruckenstein, 1991</td>
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<td>Flotation/coprecipitation</td>
<td>Metal ions</td>
<td>Almost complete separations could be achieved for all the tested cations such as U, Ce, Zn and Be from aqueous media by aluminium hydroxide as a coprecipitant and either NaLS or Gl as a collector</td>
<td>Shakir et al., 1991</td>
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<td>Adsorption on modified bone-gelatin beads</td>
<td>Cu</td>
<td>Maximum removal is achieved as a function of pH.</td>
<td>Peterson et al., 1990</td>
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<td>I on exchange on exchanger AMP)</td>
<td>Mo and W</td>
<td>Preferential sorption of Mo and W was detd. at pH 2-5 and ~10, respectively. The possibility of Mo separation from W with efficiency of 40-50% was demonstrated.</td>
<td>Zhuravlev, 1990</td>
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<td>Adsorption by Sewage sludge treated soil</td>
<td>Cd</td>
<td>Adsorption of Cd by sewage sludge amended soil was maximum as compared to adsorption by untreated soil. Addition of organic matter enhanced the Cd adsorptive capacity of the soil.</td>
<td>Szymura et al., 1990</td>
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<td>Precipitation</td>
<td>Co(III)</td>
<td>The separation of Co(III) from aqueous solution was accomplished with Nitroso derivatives of alkylresorcinols (new reagents).</td>
<td>Johannes and Medler, 1990</td>
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<td>Ion exchange (Cation Fe, Co, Ni and Cu exchanger column)</td>
<td></td>
<td>The separation of Fe, Co, Ni and Cu from pt-group metals occurred at pH 2 and the presence of 0.5 M NaCl. Besides, the recovery of Rh was &gt;98%.</td>
<td>Jiang and Huang, 1991</td>
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<tr>
<td>Adsorption by Cocoa growing solids</td>
<td>Cd</td>
<td>Studies have shown the effect of soil organic matter on Cd adsorption in four Malaysian Cocoa soils. Sorption capacities increases with the destruction of organic matter in three Malaysian soils.</td>
<td>Low and Lee, 1991</td>
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<td>Adsorption by Commercial Tea</td>
<td>Cd, Pb and Sr</td>
<td>Maximum removal was achieved. The adsorption percentage of Cd and Pb is more by undried tea than dried tea.</td>
<td>Zhao and Gao, 1991</td>
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<tr>
<td>Precipitation</td>
<td>Cd, Co and Ni</td>
<td>The elements were pre-concentrated and separated from the bulk of the matrix by outline copptn. with the hexamethylene ammonium hexamethylene dithiocarbamate iron(II) chelate complex in a flow injection system.</td>
<td>Welz et al., 1991</td>
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<td>Adsorption by oxic sediment</td>
<td>Cd</td>
<td>Maximum removal occurred at the pH range of 4.5-7. Adsorption is dependent upon pH. Very low adsorption occurred below the pH 3 and above 8.5 respectively.</td>
<td>Fu and Allen, 1992</td>
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<td>Adsorption by clay minerals and soils</td>
<td>Cr</td>
<td>Lithium is extracted from spodumene by high temperature ion exchange. Maximum removal has been obtained. Efficient removal and recovery was achieved from aqueous solution.</td>
<td>Wu and Lu Wenyai, 1991, 10(2), 19-23</td>
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<td>Ion exchange (with molten KCl)</td>
<td>Li</td>
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<td>Mahi and Fray, 1990</td>
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<td>Adsorption on alumina or silica</td>
<td>Cr(III) ions</td>
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<td>Zaki et al., 1992</td>
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<td>Adsorption on manganese dioxide</td>
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<td>Ion exchange (with potassium cobalt hexacyanoferrate(II))</td>
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<td>Bangarh et al., 1992</td>
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<td>Competitive adsorption by soils (rice paddy soil)</td>
<td>Cd and Zn</td>
<td>Addition of Zn affects the Cd²⁺ adsorption</td>
<td>Wu and Lu, Guofu 1991, 10(8), 20-3</td>
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<td>Fe, Al, Cr</td>
<td>Selective recovery of Fe, Al and Cr from sulfate tannery wastes was achieved by using ion exchangers Duolite A-7 and Purolite C 160 separately.</td>
<td>Petruzelli et al., 1991, 272-80</td>
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<td>Adsorption on soil</td>
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<td>Various soils were tested for Cu adsorption but the maximum adsorption occurred on rhizosphere soils.</td>
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<td>Successful separation of barium and other alkaline earth metal ions from aqueous solution is achieved.</td>
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<td>Adsorption on activated charcoal</td>
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<td>Maximum adsorption occurred at pH-8. Adsorption is also enhanced in presence of CaCO₃ content and clay particles (&lt;0.01 mm diameter)</td>
<td>Wu et al., 1991</td>
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<tr>
<td>Ion exchange</td>
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<td>Adsorption by phosphorylated wood</td>
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<td>Adsorption by the phosphorylated todomatsu and Shinanoki were 50 times and 20 times more, respectively, than those of untreated wood powders.</td>
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<td>Petruzzelli et al., 1991, 383-8</td>
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<td>Cd, Metals</td>
<td>Removal and recovery of Cr was achieved from chrome liquor (Tannery effluents). Activated charcol was however, proved to be the best adsorbent. Metals are extracted from a sludge containing coarse particles with an ion exchange resin in a multistage system. Adsorption of Cu on colloidal iron(III) hydroxide in soln. of total ammonia (0.14-1.2M) was performed at various pH. The max. efficiency of adsorption occurs when the sum of the fractions of the species Cu(NH$_3$)$_2^+$, Cu(NH$_3$)$_3^{2+}$ in the solutions reaches its maximum.</td>
<td>Kannan and Vijayaraghavan, 1992; Voloshchuk et al., 1992; Luo and Huang, 1992</td>
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<td>Adsorption by China clay</td>
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<td>Cd uptake was maximum (86.6%) at pH 9.5 (solution concentration 0.5x10^{-4} M at 30^oC).</td>
<td>Sharma et al., 1992</td>
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<td>Ion exchange</td>
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<td>The sepn. and recovery of metal ion is acheived through ion exchange columns at high pressure. The process is primarily intended for treatment of rare earth ores for recovery of rare earth metals.</td>
<td>Yamamoto et al., 1993</td>
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<td>Adsorption on Peat</td>
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<td>Maximum removal of Cd 95% and Cr 53% was achieved from wastewater at 21^oC and at pH 4-5 with equil. time of 2h.</td>
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<td>Adsorption on burned clay and soil (C black) and pesticides</td>
<td>Ni^{2+}, Pb^{2+}, NO_{3}^{-}, HPO_{4}^{2-}</td>
<td>The tested material showed an adsorption capacity comparable to activated carbon.</td>
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<td>ash</td>
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<td>Adsorption on natural Zeolites</td>
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<td>Chmielewska and Lesny, 1992</td>
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<td>Adsorption on bottom ash</td>
<td>Cu and Pb</td>
<td>Maximum removal of individual metals was, Cu 99.8% and Pb 92.3%. The method is very convenient.</td>
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<td>Adsorption by coconut shell carbons.</td>
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<td>Efficient removal was obtained in equil. time of 70 minutes max. and at a lower pH.</td>
<td>Rao et al., 1992</td>
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<td>Adsorption on porous polymeric beads</td>
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<td>Metals such as Cu, Cd, Zn, Pb and Hg were effectively removed from wastewater by polymeric beads. Adsorbed metals were removed from the beads using dil. mineral acids.</td>
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<td>Adsorption on various types of soils</td>
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<td>Soils with higher silt clay adsorbed a greater amount of Pb as compared to sandy soils.</td>
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<td>Ion exchange by Zirconium selenite</td>
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<td>Hydroxide Precipitation</td>
<td>Heavy metals</td>
<td>Effective removal of heavy metals is achieved from a complex wastewater matrix by hydroxide precipitation.</td>
<td>Ritz and Jekel, 1994</td>
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<tr>
<td>Adsorption on activated carbon</td>
<td>Cr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Cr&lt;sup&gt;3+&lt;/sup&gt; is removed to an appreciable extent from aq. solution by activated carbon. The method is pH dependent.</td>
<td>Leyva-Ramos et. al., 1995</td>
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<tr>
<td>Precipitation (using FeS generated in Situ)</td>
<td>Cr</td>
<td>Efficient removal of chromium is accomplished from electroplating effluents by the sulfide process.</td>
<td>Mudakavi et al., 1995</td>
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<td>Ion exchange</td>
<td>Metals</td>
<td>Recovery of metals is achieved from an acid containing metal salt solution by an ion exchanger.</td>
<td>Froehlich et al., 1995</td>
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<tr>
<td>Adsorption</td>
<td>Cr(VI)</td>
<td>Maximum removal of Cr(VI) is obtained from wastewater with α-alkaline iron oxide. The spent iron oxide is regenerated using 0.5 molL&lt;sup&gt;-1&lt;/sup&gt; H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;.</td>
<td>Wu et. al., 1994</td>
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<tr>
<td>Precipitation</td>
<td>As</td>
<td>The wastewater from tin ore smelting untreated with lime milk and Fe(II) for effective as removal as insol. arsenates or arsenites.</td>
<td>Zhu et al., 1992</td>
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<td>Adsorption by biogas residual slurry</td>
<td>Cr(VI)</td>
<td>Effective removal of Cr(VI) is achieved from aq. soln. by waste biogas residual slurry at pH 1.5</td>
<td>Namasivayam and Yamuna, 1995</td>
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<td>Ion exchange</td>
<td>Cd and CN⁻</td>
<td>The transformation of resin from Cr⁺ form into CdCl₂⁻ form which improve its adsorbing capacity and the subsequent recovery of Cd and CN⁻ from wastewater.</td>
<td>Li, 1994</td>
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<td>Adsorption/ co-precipitation</td>
<td>Sb(V) and (III)</td>
<td>Removal of antimony(V) and (III) from aqueous solution by flocculation with ferric salts in the presence of different inorganic compounds.</td>
<td>Enders and Jekel, 1994, 135(II)</td>
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<tr>
<td>Precipitation</td>
<td>Sb(V) and (III)</td>
<td>Good Sb(V) and (III) removal is achieved from aqueous solutions by sulfide precipitation followed by flocculation with trivalent iron salts.</td>
<td>Enders and Jekel, 1994, 135(12)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Cr(VI)</td>
<td>Maximum removal of Cr(VI) is accomplished from wastewater using adsorbent based on bagasse and coconut jute. Removal in general is most effective at low pH and activated coconut jute is most active among the four adsorbent studies.</td>
<td>Chand et al., 1994</td>
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<tr>
<td>Ion exchange (using ion exchange resins)</td>
<td>Ni²⁺</td>
<td>Recovery of Ni is effectively achieved from nickel coating wastewater with ion exchange resin.</td>
<td>Kobayashi and Aoki, 1995</td>
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<tr>
<td>Adsorption by peanut hull carbon</td>
<td>Pb(II)</td>
<td>Efficient removal of Pb(II) is accomplished from aqueous solution by carbon prepared from peanut hulls (PHC)</td>
<td>Periasamy and Namasivayam, 1995</td>
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<tr>
<td>Precipitation</td>
<td>As</td>
<td>The removal of arsenic is achieved from wastewater by precipitation in oxidized Fe-As system.</td>
<td>Zhao, 1995</td>
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<td>Adsorption/ Microfiltration</td>
<td>As</td>
<td>The removal of arsenic is achieved is performed from contaminated water with the adsorption on to finely dispersed activated alumina followed by microfiltration.</td>
<td>Moetazavi et al., 1993</td>
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<td>Adsorption by treated activated charcoal</td>
<td>Zn(II)</td>
<td>Remarkable removal of Zn(II) ion and its complexes is achieved from solution by activated charcoal treated by the oxidn. neg. ionizing (OA) method to produce more O-contg. surface group.</td>
<td>Mu and Yang, 1995</td>
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<tr>
<td>Biosorption by Zogloea ramigera</td>
<td>Pb(II),Cu(II),Ni(II) and Fe(III)</td>
<td>The maximum biosorption of Pb(II), Ni(II) and Cu(II) was detd. at 4.0-4.5 whereas for Fe(III) max. biosorption was at pH 2.0. The optimum temperature for Cu(II) biosorption was 25°C while for Pb(II) and Fe(III) was 25-45°C.</td>
<td>Sag et al., 1995</td>
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<tr>
<td>Adsorption on polymerized dust</td>
<td>Hg(II)</td>
<td>Max. accumulation was noted within 4h; max. removal (54%) was recorded at &lt;10 mgL⁻¹ Hg(II). The sorbent is effective at pH 3.5-8.5. Hg(II) could be released by using 1M HCl or chelating agent (0.1 M EDTA).</td>
<td>Raji et al., 1996</td>
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<tr>
<td>Adsorption on polys electrolytes</td>
<td>Heavy metal</td>
<td>A dosage 5 mgL⁻¹ was adequate to achieve 65% COD removal, 97% suspended solid and 90% heavy metal removal.</td>
<td>Kori et al., 1994</td>
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<td>Adsorption by using rejection shot blast fines</td>
<td>Cadmium, Zinc and Lead</td>
<td>Adsorption capacity is greatest for lead, followed by zinc and cadmium. Adsorption of metal is sensitive to pH.</td>
<td>Smith et. al., 1995</td>
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<td>Adsorption on C. crispata</td>
<td>Cu(II)</td>
<td>Increase of biomass quantity or the decrease of Vo/x ratio affected the quantities of Cu removal from aq. solution.</td>
<td>Ozer et al., 1995</td>
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<td>Adsorption on manganese zinc ferite powder</td>
<td>Zn(II)</td>
<td>Adsorption was most affective between pH 9-11.</td>
<td>Tikhomolova et al., 1995</td>
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<td>Adsorption on polyacrylamide grafted tin(IV) oxide gel</td>
<td>Pb(II)</td>
<td>Uptake is maximum around pH 5.5 Spent adsorbent can be regenerated by acid treatment and reused.</td>
<td>Subha et al., 1996</td>
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<td>Adsorption on Fe(III)/Cr(II) hydroxide</td>
<td>As(III), Hg(II), Cr(II)</td>
<td>Removal was efficient.</td>
<td>Namasivayam et al., 1995</td>
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<tr>
<td>Adsorption on calcium hydroxyapatite</td>
<td>Cd(II)</td>
<td>Adsorption increases with pH.</td>
<td>Jeanjean et al., 1995</td>
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<td>Adsorption on magnetite pellets</td>
<td>Zn(II)</td>
<td>Pellet size and reaction time had a significant impact on adsorption capacity.</td>
<td>Cargnel et al., 1995</td>
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<tr>
<td>Adsorption by Qitaihe weathering coal humic acid</td>
<td>Cd(II)</td>
<td>Proved efficient for removal of Cd(II).</td>
<td>Ming et al., 1995</td>
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<td>Sorption by a natural wetland</td>
<td>Cd, Cu, Pb and Zn</td>
<td>Result support the proposal to construct a wetland planted with selected species of macrophytes.</td>
<td>Mangur et al., 1995</td>
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<td>Reduction by modified wood flour</td>
<td>Cr(VI)</td>
<td>The redn. rate of Cr(VI) is &gt;99.5 when contact time is &gt;6 minute.</td>
<td>Xie et al., 1995</td>
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<td>Sorption on peat</td>
<td>Pb, Ni, Fe, Mn, V, Mo and Cr</td>
<td>Almost complete removal was obtained.</td>
<td>Naumova et al., 1995</td>
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<td>Adsorption by pyrolysite</td>
<td>Pb$^{2+}$, Zn$^{2+}$ and Mg$^{2+}$</td>
<td>Adsorption of the metal ions followed the order Pb$^{2+}$ &gt; Zn$^{2+}$ &gt; Cd$^{2+}$. 100% and 96% removal of lead have been achieved from synthetic waste water contg. 5 mgL$^{-1}$ and 120 mgL$^{-1}$ of Pb$^{2+}$ resp. at pH 7.</td>
<td>Ajmal et al., 1995</td>
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<tr>
<td>Adsorption on xanthate</td>
<td>Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$, Cr$^{6+}$</td>
<td>Was efficient for complete removal.</td>
<td>Yang et al., 1995</td>
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<tr>
<td>Reduction by coffee waste</td>
<td>Cr(VI)</td>
<td>Reduction depends on the mass of coffee wastes, temp. and sulphuric acid conc.</td>
<td>Kauspediene et al., 1995</td>
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<tr>
<td>Biosorption, elution and electrodialysis by biomass</td>
<td>Cd</td>
<td>The Cd conc. in the aq. solution can be reduced to very low levels (~10 µgL$^{-1}$).</td>
<td>Butter et al., 1995</td>
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<tr>
<td>Biosorption with dry biomass</td>
<td>Ni(II)</td>
<td>The biomass removes the Ni$^{2+}$ by ion exchange with surface H$^+$.</td>
<td>Schneider et al., 1994</td>
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<td>Adsorption by bark of L. Sibirica laden, P. sylvestris and A. siberia laden</td>
<td>Cu(II)</td>
<td>Most favourable pH values lies within the ranges of 6.5-11.0.</td>
<td>Loskutor et al., 1995</td>
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<td>Adsorption using recycled iron-bearing material</td>
<td>Pb, Zn and Cd</td>
<td>Adsorption capacity was in the order of Pb&gt;Zn&gt;Cd. Adsorption is sensitive to pH. More than 90% removal occurring within 10-20 h.</td>
<td>Smith et al., 1995</td>
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<tr>
<td>Adsorption on peanut hull carbon</td>
<td>Copper</td>
<td>Quant. removal of Cu(II) from a soln. contg. 20 mg Cu(II)\text{L}^{-1} \text{by 0.9g PHC per L was obsd. in the pH 4.0-10.0}</td>
<td>Periasamy et al., 1996</td>
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<tr>
<td>Adsorption on zeolitized waste materials</td>
<td>Cu(II), Zn(II)</td>
<td>Removal of metal ions vs. time has been studied.</td>
<td>Patane et al., 1996</td>
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<td>Biosorption by SR$_4$ bacteria</td>
<td>Ni$^{2+}$</td>
<td>Removal was &gt;99% at temp. 20-40°C, pH 9...</td>
<td>Wu et al., 1995</td>
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<td>Sorption by natural moss</td>
<td>Cr(III), Cr(VI)</td>
<td>Max. sorption capacities was 18.9 and 7.1 mgg$^{-1}$ for Cr(III) and Cr(VI) respectively.</td>
<td>Lee et al., 1995</td>
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<tr>
<td>Adsorption on silica-immobilized Medicago sativa (alfalfa)</td>
<td>Cu(II)</td>
<td>Cu binding the different alfalfa occurred within 5 min. pH is sensitive in removal. Deospriton is possible with 0.1 M HCl.</td>
<td>Gardea, Torresdey et al., 1996</td>
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<td>Adsorption on inorganic ion exchanger</td>
<td>Cr(III)</td>
<td>Adsorption capacity of ion exchanger decreased in the order Al₂O₃ &gt; Synthetic TiO₂ &gt; com. nnatase TiO₂ = Smectile) com. rutile TiO₂ &gt; SiO₂</td>
<td>Chen et al., 1996</td>
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<tr>
<td>Biosorption by streptomyces pimprine</td>
<td>Cd(II)</td>
<td>Rate of uptake was max. in the first 10 min. and the equil. achieved after 60 minute. Max. adsorption was observed at pH 5. 0.1M EDTA sol. could desorb Cd loaded.</td>
<td>Puranik et al., 1995</td>
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<tr>
<td>Adsorption on minerals</td>
<td>Cd, Cr(III), Cr(VI), Hg and Pb</td>
<td>Result were quantified by pH values at which 10, 50 and 90% of metal uptake occurred. Adsorption was strongly dependent on org. content of the material.</td>
<td>Arnfalk et al., 1996</td>
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<tr>
<td>Adsorption reduction on natural polymers</td>
<td>Cr(VI)</td>
<td>Process is pH dependent.</td>
<td>Bosinco et al., 1995</td>
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<td>Adsorption on nematite feldspar</td>
<td>As(V)</td>
<td>pH of the system played keyrole in uptake. The max. removal was 100% with hematite and 97% with feldspar.</td>
<td>Singh et al., 1996</td>
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<td>Biosorption by canola meal (cm)</td>
<td>Cr(III)</td>
<td>Chromium adsorption increased with temp. between 40 and 50. pH between 5 and 7 did not have much effect on adsorption.</td>
<td>Al-Asheh et al., 1996</td>
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<td>Adsorption by phosphate treated saw-dust</td>
<td>Cr(VI)</td>
<td>Adsorption of Cr(VI) was 100% at pH &lt;2 for the initial Cr(VI) conc. of 8-50 mgL⁻¹. Phosphate treated saw dust recovered (87%) using 0.01% M Sod hydroxide.</td>
<td>Ajmal et al., 1996</td>
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<td>Sorption on palm pressed fibers</td>
<td>Cu(II), Ni(II)</td>
<td>Homogeneous column studies show that metal sorption increased with lower flow rate, higher bed depth and lower metal-ion conc.</td>
<td>Tan et al., 1996</td>
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<td>Ultrafiltration</td>
<td>Cd(II), Cr(VI)</td>
<td>By adjusting operation parameters the conc. of Cd and Cr were decreased by factors of 500 and 300 respectively.</td>
<td>Zaoug et al., 1995</td>
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<td>Adsorption on granular activated carbon</td>
<td>Cr(VI)</td>
<td>Most effective pH was 2.5-3.0 and max. adsorption capacity was 145 mgg⁻¹.</td>
<td>Sharma et al., 1996</td>
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<td>Bisorption by chickpea feather</td>
<td>Au, Pt and Pd</td>
<td>Gold(III) potassium cyanide was accumulated upto 5.5% at pH 2.0. Expts. suggested C-feather is promising for use in removable/recovery of precious metals.</td>
<td>Suyama et al., 1996</td>
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<td>Adsorption on pre-treated neutral zeolite material</td>
<td>Hg(II)</td>
<td>The mercury(II) uptake by the zeoliferous rock found to be higher than of the hendidte and reached 43.0 mgg⁻¹ and for henlandite was found to be 16.3 mgg⁻¹.</td>
<td>Misaelides et al., 1995</td>
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<td>Sorption on hexane-extracted spent bleaching earth</td>
<td>Cr(III)</td>
<td>Max. sorption was calculated to be 9.48 mgg⁻¹ at room temperature.</td>
<td>Low et al., 1996</td>
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<td>Adsorption on granular activated carbon</td>
<td>Pb(II)</td>
<td>Column pH was extremely important to Pb removal in GAC column. Simple acid-base regeneration procedure effectively desorbed/resolubilized C-bond Pb.</td>
<td>Reed et al., 1996</td>
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<td>Adsorption on Iron(III)-loaded chelating resin</td>
<td>As(III), As(V)</td>
<td>As(V) was strongly adsorbed to the resin in the pH 2-4, while As(III) was moderately adsorbed at pH 8-10. Regeneration of the resin was carried out with 0.1 mol/dm³ NaOH solutions.</td>
<td>Matsunaga et al., 1996</td>
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<td>Adsorption on activated carbon</td>
<td>Cd(II), Zn(II)</td>
<td>Cd and Zn removal increased on raising pH and temp; and decreased on raising the molar metal/carbon ratio.</td>
<td>Marzel et al., 1996</td>
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<td>Adsorption on iron oxide-coated granular activated carbon</td>
<td>Cu(II), Cd(II)</td>
<td>Efficient removal and recovery was observed.</td>
<td>Wang et al., 1995</td>
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<td>Adsorption on flyash</td>
<td>Cr(VI)</td>
<td>Better sep. is obtained at acidic pH and at higher temp. Particle size has no significant effect on separation.</td>
<td>Dasmahapatra et al., 1996</td>
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<td>Biosorption by non-living water hyacinth roots</td>
<td>Heavy metal</td>
<td>Good adsorption was recorded.</td>
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<td>Appalaction bituminous flyash was potential adsorbent for removal of Pb(II).</td>
<td>Laumakis et al., 1995</td>
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<td>Adsorption on Zeolite</td>
<td>Ni(II), Cr(III)</td>
<td>Using zeolite in the Na or H form it is possible to ext. almost complete nickel ions and upto 70% of Cr(III) ions.</td>
<td>Gomonai et al., 1996</td>
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<td>Biosorption using crude shrimp chitin</td>
<td>Cu(II), Cr(III), Ni(II)</td>
<td>The shrimp chitin demonstrated remarkable Cu(II) and Cr(III) collecting of over 95% and 96% resp. Desorption is done with 0.1 M EDTA.</td>
<td>Chui et al., 1996</td>
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<td>Adsorption on activated carbon</td>
<td>Ag(II)</td>
<td>Adsorption capacity of carbon of silver reached 3.5 mgg⁻¹. With increase in silver conc. the adsorption capacity of a carbon also increases. The optimum pH of wastewater was 5.</td>
<td>Jiang et al., 1996</td>
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<td>Adsorption on blast furnace sludge</td>
<td>Cu(II)</td>
<td>Good adsorbent for Cu²⁺ removal.</td>
<td>Lopez et al., 1996</td>
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<td>Bisorption on Rhizopus nigricans</td>
<td>Pb(II)</td>
<td>The efficiency of adsorption of Pb²⁺ and the soln. capacity at flow rates 0.275 BV/min was 83.6% and 49 mgg⁻¹ resp. regeneration is possible with CaCl₂ solns.</td>
<td>Zhang et al., 1995</td>
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<td>Adsorption on manganese-oxide-coated composite adsorbent</td>
<td>Cu(II), Cd(II)</td>
<td>Good result are obtained.</td>
<td>Fan et al., 1996</td>
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<td>Ion exchange</td>
<td>Cu(II)</td>
<td>Effect of contact time and the nature of anionic species on the efficiency of Cu removal was studied.</td>
<td>Ulmanu et al., 1996</td>
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<td>Exchange using zeolite and dionyl naphthalene sulfonate</td>
<td>Zn²⁺, V²⁺, Cd²⁺ and Hg²⁺</td>
<td>NaDNSS has advantages over zeolite NaA for exchange of different metals.</td>
<td>Sayed et al., 1996</td>
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<td>Sorption on biomass and silica immobilized biomass of Medicago sativa (alfalfa)</td>
<td>Ni(II)</td>
<td>Optimal pH for removal was 5-6. 80% of the nickel ions bound to alfalfa plant tissue in less than 5 min. 90% of the retained nickel was recovered with 0.1M HCl solns.</td>
<td>Gardea et al, 1996</td>
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<td>Adsorption on china clay</td>
<td>Cd(II), Ni(II)</td>
<td>78% of Cd and 86% of Ni were recovered by 1g of China clay form 50 cm³ of 5.62 mgL⁻¹ at 30°C and pH 6.5.</td>
<td>Sharma et al., 1996</td>
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<td>Adsorption by Albizia Labbeck pod</td>
<td>Cr</td>
<td>The optimum pH for adsorption was found to be 2.0. The metal removal efficiency was 94 to 99%</td>
<td>Verma et al., 1996</td>
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<td>Biosorption on waste biomass</td>
<td>Zn(II)</td>
<td>The adsorption ratio was rapid during the initial 5 min and equil. was achieved within 2h.</td>
<td>S.P. et al., 1996</td>
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<tr>
<td>Biosorption on waste biomass</td>
<td>Cu(II)</td>
<td>The uptake Cu increase with pH and max. uptake was observed at pH 5. The uptake capacity of waste biomass (mg Cu/g biomass) decreased with increases in biomass and as much as 90% Cu uptake could be achieved.</td>
<td>Modak et al., 1995</td>
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<td>Adsorption on Salvinia natans</td>
<td>Pb(II), Cd(II), Ni(II), Cu(II), Cr(V) and Hg(II)</td>
<td>Removal capacity is in order of Cu(II) &gt; Ni(II) &gt; Pb(II) &gt; Cd(II) &gt; Hg(II) &gt; Cr(VI)</td>
<td>Sen et al., 1994</td>
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<td>Biosorption on Penicillium</td>
<td>Cu</td>
<td>Higher pH had a positive effect and higher temp. had a negative effect on adsorption. Cu adsorption decreased in presence of Ni.</td>
<td>Mishra et al., 1996</td>
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<td>Batch adsorption by using porous cellulose carrier modified polyethyleneimine</td>
<td>Hg(II)</td>
<td>Selectively remove Hg even at acidic regions. Extensive crosslinking of PE, chains that restrict ligand mobility was cited as the foremost factor controlling the adsorption.</td>
<td>Navarro et al., 1996</td>
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<tr>
<td>Adsorption by decaying leaves of plant (Platnus orientalis)</td>
<td>Cr$^{6+}$, Ni$^{2+}$</td>
<td>The max. removal for Cr$^{6+}$ is 7.5-8.0 gKg$^{-1}$ leaves at pH 4.0 and for Ni$^{2+}$ about 2.6 gKg$^{-1}$ at pH 5.0-5.5.</td>
<td>Tan et al., 1996</td>
</tr>
<tr>
<td>Bisorption by marine algae Ecklonia radiata</td>
<td>Pb, Cd and Cu</td>
<td>Pb sorption capacity was particularly marked. At pH 4.5-5.5 the Pb uptake capacity of E. radiata was 1.36 mMg$^{-1}$ (282 mgg$^{-1}$) much higher than others. Pb sorption increased, reaching a plateau at pH 5.</td>
<td>Matheickal et al., 1996</td>
</tr>
<tr>
<td>Adsorption on agricultural byproducts</td>
<td>Cd$^{2+}$ and Pb$^{2+}$</td>
<td>Cd$^{2+}$ follows the order polymd. onion skin &gt; bagasse &gt; banana husk &gt; suffola husk &gt; spinach. Adsorption of Pb$^{2+}$ follows the order polymd onion skin &gt; spinach &gt; suffola husk &gt; bagasse &gt; banana husk. Polymd. onion shows max. adsorbing capacity for both.</td>
<td>Jahagirdar et al., 1997</td>
</tr>
<tr>
<td>Adsorption by algal biomass</td>
<td>Cu(II), Zn(II)</td>
<td>Recovery of metal from algae was higher by acidic or neutral than in alk. conditions. Cu(II) ion is removed relatively higher than Zn(II) ions.</td>
<td>Park et al., 1996</td>
</tr>
<tr>
<td>Sorption by algae and algae byproducts</td>
<td>Heavy metals</td>
<td>Sorption isotherm showed increasing sorption capacity and decreasing sorption efficiencies with increase in initial metal conc. pH decisively controlled sorption (pH 3-7) and desorption (pH 1-2).</td>
<td>Sandau et al., 1996</td>
</tr>
<tr>
<td>Adsorption onto granular activated carbon</td>
<td>Cd and Zn</td>
<td>Cd and Zn removal increased with pH and decreased with molar metal/C ratio.</td>
<td>Gabaldon et al., 1996</td>
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<tr>
<td>Adsorption on aluminosilicate</td>
<td>Zn</td>
<td>Zeolite A, mixture of different aluminosilicates with ~39% SiO₂ and montmorillonite to remove Zn²⁺ from waste water.</td>
<td>Dosensver et al., 1996</td>
</tr>
<tr>
<td>Biosorption by dead biomass (e.g. Streptomyces)</td>
<td>Cd(II)</td>
<td>Clavulanic acid is promising for Cd removal.</td>
<td>Matis et al., 1997</td>
</tr>
<tr>
<td>Adsorption by agricultural solid waste (Coir pith carbon)</td>
<td>Cu(II)</td>
<td>Adsorption equilibrium was reached in 25 min. for 20-50 mg/L conc. of Cu(II). The % removal increased from 50 to 90 with the increase of pH from 20 to 40 and remained constant to pH 10.0 for Cu(II) concentration of 20 mg/L.</td>
<td>Namasivayam et al., 1997</td>
</tr>
<tr>
<td>Sorption by microalgae</td>
<td>Cd</td>
<td>(50 L) with Cd resistant cells of Chlorella vulgaris removed ~40% of added Cd from a 10 mg CdL⁻¹ solutions within 7 days.</td>
<td>Sandau et al., 1996</td>
</tr>
<tr>
<td>Sorption by magnetite immobilized cells of Enterobacter sp. 4-2</td>
<td>Ni²⁺</td>
<td>Under selected conditions (temp. at 25° and net time of 10 min) 50-90% of Ni²⁺ was removed by immobilized cells at pH 7-9. Complete recovery was possible with dil. citric acid.</td>
<td>Wong et al., 1997</td>
</tr>
<tr>
<td>Adsorption by seaweeds and their derivatives</td>
<td>Copper, Nickel, Zinc, Cadmium</td>
<td>The effect of the presence of more than one metal ion in solution was investigated in order to determine whether any competitive effect might have effected metal ion uptake.</td>
<td>Aderhold et al., 1996</td>
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<tr>
<td>Adsorption by Fe(III)/Cr(III) hydroxide</td>
<td>Hg(II)</td>
<td>Almost complete removal of Hg(II) from a solution containing 40 mgL(^{-1}) in a 50 ml solution by 175 mg of adsorbent occurred at an initial pH of 5.8. Desorption was observed 65% in 2% KI.</td>
<td>Namasivayam et al., 1997</td>
</tr>
<tr>
<td>Adsorption of activated carbon</td>
<td>Cu and Ni</td>
<td>Metal removals increase on raising the pH and temperature and decrease on raising the initial metal concentration at constant carbon dose.</td>
<td>Secco et al., 1997</td>
</tr>
<tr>
<td>Adsorption by Zeolitized waste minerals</td>
<td>Cr(III)</td>
<td>The Cr removal under legal limit in the waste water (2 mg/ dm(^{3})) is achieved in short time.</td>
<td>Patane et al., 1996</td>
</tr>
<tr>
<td>Adsorption by spent plastic etchants</td>
<td>Cd(VI)</td>
<td>Achieved 100% Cr(VI) removal.</td>
<td>Yudina et al., 1996</td>
</tr>
<tr>
<td>Adsorption by rice husk</td>
<td>Cr, Zn, Cu &amp; Cd</td>
<td>At the optimal conditions the Cr, Zn, Cu and Cd removal were 79, 85, 80 and 85% respectively. Almost complete elution with dil. HCl.</td>
<td>Munaf et al., 1997</td>
</tr>
<tr>
<td>Adsorption and membrane filtration</td>
<td>Arsenic</td>
<td>The effect of different parameters such as pH, residue time and adsorbent characteristic were studied. Regeneration was also done.</td>
<td>Mortazari et al., 1995</td>
</tr>
<tr>
<td>Adsorption by sepiolite</td>
<td>Zn</td>
<td>Zn(^{2+}) retention by the sepiolite bed becomes limited, but not abolished by repeated regeneration with Na(^{+}) solutions at increasing concentration.</td>
<td>Brigatti et al., 1996</td>
</tr>
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<tr>
<td>Sorption on soil treated with sewage sludge supernatant</td>
<td>Cd, Cu, Ni, Zn, Pb and Cr</td>
<td>Selectivity between metals resulted in the following metal affinities based on their Kd values: Pb &gt; Cu &gt; Zn &gt; Ni &gt; Cd-Cr at pH 4.5 and Pb &gt; Cu &gt; Zn &gt; Cd &gt; Ni &gt; Cr at pH 6.5.</td>
<td>Gao et al., 1997</td>
</tr>
<tr>
<td>Biosorption by seaweeds and seaweeds derivatives</td>
<td>Cu, Ni, Cd, Pb and Zn</td>
<td>The 3 brown seaweeds can remove the Cu, Ni, Cd, Pb and Zn in considerable amount.</td>
<td>Williams et al</td>
</tr>
<tr>
<td>Biosorption by alginate immobilized Anabena variabilis</td>
<td>Lead</td>
<td>A removal of 96% was achieved at 2 ppm concentration of lead ions with 0.25 gm of biomass after agitation for an hour at pH 6-9. The presence of other ions like Cl-, acetate, SO₄²⁻ and carbonate decreased the biosorption.</td>
<td>Verma et al., 1996</td>
</tr>
<tr>
<td>Adsorption by modified bark</td>
<td>Pb²⁺, Zn²⁺, Cr²⁺, Fe²⁺, and Cu²⁺</td>
<td>The metal ions could be stripped by addition of 0.1 N HCl, making the subs. regeneration and its reutilization possible rate.</td>
<td>Gloguen et al., 1997</td>
</tr>
<tr>
<td>Sorption by moss</td>
<td>Cr(III)</td>
<td>The maximum sorption capacities were 15.4 and 13.7 mg L⁻¹ for synthetic solution and tannery wastewater.</td>
<td>Low et al., 1997</td>
</tr>
<tr>
<td>Sorption by activated slag a blast-furnace waste</td>
<td>Pb and Cr</td>
<td>The uptake of Pb is found to be greater than that of Cr. Experiments were performed to recover Pb²⁺ and chemical regeneration of the spent slag column in situ.</td>
<td>Srivastava et al., 1997</td>
</tr>
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<tr>
<td>Adsorption on treated and untreated low grade bituminous coal</td>
<td>Cu(II), Ni(II), Zn(II) and Cr(VI)</td>
<td>Bituminous coal was subjected to hydrothermal treatment to enhance the adsorption of Cu(II), Ni(II), Zn(II) and Cr(IV).</td>
<td>Singh et al., 1997</td>
</tr>
<tr>
<td>Adsorption by immobilized phytic acid</td>
<td>Cd, Cu, Pb, Ni and Zn</td>
<td>6.6 mg Cd^{2+}, 7 mg Cu^{2+}, 7.2 mg Ni^{2+}, 7.4 mg Pb^{2+}, and 7.7 mg Zn^{2+} can be adsorbed by each gram of PVP-phytic acid complex.</td>
<td>Tsao et al., 1997</td>
</tr>
<tr>
<td>Adsorption on sugar cane bagasses</td>
<td>Copper</td>
<td>The adsorption equil. was attained in 8 h at room temperature.</td>
<td>Filho et al., 1996</td>
</tr>
<tr>
<td>Sorption on fibrous sorbent (i.e. AN-1 and Kopan-10,60)</td>
<td>Cr, Cd, Zn and Cu</td>
<td>AN-1 Kopan-10, Kpan-60, Kpan-90, Kpan-150 and Ampan polyampholytes showed a firly high effectiveness for removal of Cr, Cd, Zn and Cu.</td>
<td>Burinski S.V., 1996</td>
</tr>
<tr>
<td>Sorption on Usar (Reh)' soil</td>
<td>Ni(II) and Cr(III)</td>
<td>The max. removal of Ni and Cr is obtained at pH 7.0 and 6.0 resp. The results indicate that 100% removal is possible by this method. As the concn. of Ni and Cr increases the removal is also enhanced.</td>
<td>Singh et al., 1997</td>
</tr>
<tr>
<td>Biosorption on biomass Pseudomonas aeruginosa PU12</td>
<td>Lead, Copper and Cadmium</td>
<td>At pH 5.5 the resting cells were able to uptake &lt;110 mg Pb g^{-1} dry cell and inactivated cell can adsorb 70 mg Pb g^{-1} dry cell resulted in 98 and 82% recovery of Pb, Cu and Cd resp.</td>
<td>Chang et al., 1997</td>
</tr>
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<tr>
<td>Adsorption using zeolite tuff</td>
<td>Lead, Nickel</td>
<td>Removal capacity is considerably higher for Pb than for Ni under all conditions. The finer zeolite particles used the higher the metal exchange capacity. An initial pH of 4 is favourable for high metal removals.</td>
<td>Ali et al., 1997</td>
</tr>
<tr>
<td>Sorption on quanternized rick husk</td>
<td>Cr(VI)</td>
<td>Sorption capacity of Cr(VI) was 32.2 mg g⁻¹ at pH 4.82 and 25°C.</td>
<td>Low et al., 1997</td>
</tr>
<tr>
<td>Biosorption by algal biomass</td>
<td>Cadmium</td>
<td>HCl at pH 2 desorbed 80% of Cd initially loaded onto the biomass. Almost complete recovery of Cd was achieved by a 3.24 mM EDTA solution.</td>
<td>Chu et al., 1997</td>
</tr>
<tr>
<td>Adsorption by biomass</td>
<td>Pb²⁺</td>
<td>The uptake capacity of entrapped biomass was 121.2 mg g⁻¹. The recovery was 94%.</td>
<td>Zhao et al., 1996</td>
</tr>
<tr>
<td>Rhizopus nigricans entrapped in gelatin</td>
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<tr>
<td>Adsorption on carbonaceous adsorbent</td>
<td>Cr(VI), Cr(III) and Pb</td>
<td>Ac carbon was found to selectively adsorbed only hexavalent form of chromium. However lignin is found to adsorbed at the metals ions employed in the study.</td>
<td>Lalvani et al., 1997</td>
</tr>
<tr>
<td>Sorption on pea</td>
<td>Cd, Cu and Zn</td>
<td>Adsorption follows the langmuir isotherm.</td>
<td>Mckay et al., 1997</td>
</tr>
<tr>
<td>Adsorption by Helmoschus esculentus</td>
<td>Cr(IV)</td>
<td>The removal was most effective at low pH values. Favourable conditions are an equil. time of 7 h and an adsorbent dose of 10 mg L⁻¹.</td>
<td>Jasiia et al., 1997</td>
</tr>
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<tr>
<td>Adsorption on activated carbon</td>
<td>Cd(II)</td>
<td>The am. of Cd(II) adsorbed was reduced ~3 times by increasing the temp. from 10 to 40°C. Max. adsb. at pH 8 while it was not adsorbed at &lt;2.</td>
<td>Leyva et al., 1996</td>
</tr>
<tr>
<td>Adsorption by activated zeolite</td>
<td>Pb2+, Cd2+ and Cr3+</td>
<td>Suitable reaction conditions were as follows: NaOH concn. 3-5 molL⁻¹, temp. 95±5°C, reaction time 6-9 h and pH &gt; 4. Zeolite was recycled by washing with 0.05M HCl.</td>
<td>Hu et al., 1997</td>
</tr>
<tr>
<td>Biosorption by Phellinus badius</td>
<td>Pb(II)</td>
<td>At pH 5.0, the Pb uptake capacity of P. badius is 0.82 mmolsg⁻¹ (170 mgg⁻¹). The metal binding was 90% in 15 min.</td>
<td>Matheickal et al., 1997</td>
</tr>
<tr>
<td>Sorption on incineration fly ash in a marine clay</td>
<td>Zn, Pb, Cd, Cu and Cr</td>
<td>The soilly alk. marine clay could completely retain these heavy metals at its natural soil pH of 8.4 in acidic condition the mobility of heavy metal followed the Cd&gt;Zn&gt;Cu&gt;Pb&gt;Cr.</td>
<td>Lim et al., 1997</td>
</tr>
<tr>
<td>Adsorption by kiln dust</td>
<td>Cr, Fe, Co, Cu, Zn, Cd, Pb, Ni and Mn</td>
<td>Result showed cement kiln dust is favourable material to effectively remove industrial wastewater.</td>
<td>El Awady et al., 1997</td>
</tr>
<tr>
<td>Biosorption by biomass</td>
<td>Cd</td>
<td>Micrococeus lutens increased adsorption from 9 to 50% at the 12st contact hour.</td>
<td>Souza et al., 1997</td>
</tr>
<tr>
<td>Reduction by steel wool</td>
<td>Cr(VI)</td>
<td>CaCO₃ powder could be used as a cheap precipitate for Cr(III) ions.</td>
<td>Ozer et al., 1997</td>
</tr>
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<tr>
<td>Adsorption on activated carbon from the rice husk</td>
<td>Co(II)</td>
<td>The optimum pH, ACRH dosage and contact time were 6-7, 1.5 g ACRH/50 mL soln. and 40 min.</td>
<td>Teper et al., 1997</td>
</tr>
<tr>
<td>Sorption by non living biomass of water hyacinth roots</td>
<td>Cr(VI)</td>
<td>The optimum sorption was at pH 2 and decreased rapidly with increasing pH. The Cr(VI) uptake decrease with increasing temp. The max. sorption capacity for Cr(VI) was 8.93 mgg⁻¹ biomass and 8.92 mgg⁻¹ biosorbent.</td>
<td>Low et al., 1997</td>
</tr>
<tr>
<td>Sorption on lignin</td>
<td>Pb(II), Cr(III), Cr(VI) and Zn(II)</td>
<td>Functionalities as phenols in lignin serves as site for the metal cation exchanger. Elution of adsorbed metal is possible with 10% sulphuric acid.</td>
<td>Latvani et al., 1997</td>
</tr>
<tr>
<td>Sorption on opoka</td>
<td>Cr(III), Fe(III), Ni(II) and Cu(II)</td>
<td>Silica mineral opoka is a potential adsorbent for metal removal.</td>
<td>Nikiforov et al., 1997</td>
</tr>
<tr>
<td>Biosorption on C. vulgaris</td>
<td>Fe(III), Cr(VI)</td>
<td>Optimum biosorption pH for both metal ions was detd. as 2.0.</td>
<td>Aksu et al., 1997</td>
</tr>
<tr>
<td>Adsorption by Azolla filiculoides</td>
<td>Cr(VI)</td>
<td>Max. adsorption capacity was detd. 70.6 mgg⁻¹ at 18° and 12.2 mgg⁻¹ at 32°C, both at pH 2.</td>
<td>Zhao et al., 1997</td>
</tr>
<tr>
<td>Adsorption by natural sorbents</td>
<td>Cr(III)</td>
<td>Both bentonites and zeolites were able to remove Cr(III).</td>
<td>Smiechowski et al., 1997</td>
</tr>
<tr>
<td>Adsorption on keratinus materials (viz. Human black and white hairs)</td>
<td>Cr</td>
<td>Optimum condition for removal was 4 h and pH 1.5 resp.</td>
<td>Balasubramanian et al., 1998</td>
</tr>
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<tr>
<td>Adsorption by flyash</td>
<td>Cr(VI)</td>
<td>The optimum removal was accomplished at pH 2 with contact time of 2 h.</td>
<td>Fytianos et al., 1997</td>
</tr>
<tr>
<td>Biosorption on poly (ethyl eneimine) granular carbon</td>
<td>Cr(III)</td>
<td>Sorption capacity enhanced significantly by NaCl and Na₂SO₄, the effect being more marked on TGF sorbent which shows &gt;100% increase in Cr(III) sorption in 0.5M NaCl and 0.25M Na₂SO₄</td>
<td>Chanda et al., 1997</td>
</tr>
<tr>
<td>Adsorption onto functionalized formic lignin from sugar bagasse</td>
<td>Cd(II), Pb(II)</td>
<td>Functionalized lignin has higher binding capacity for Pb(II) than Cd(II) at pH 6.0</td>
<td>Pineda et al., 1997</td>
</tr>
<tr>
<td>Adsorption by fly ash</td>
<td>Cu(II), Pb(II), Zn(II)</td>
<td>Sorption capacity increases 40 to 100% when pH changes from 1 to 10. The removal order is Pb &gt; Cr &gt; Cu &gt; Ni &gt; Zn &gt; Cd.</td>
<td>Ricou et al., 1998</td>
</tr>
<tr>
<td>Adsorption on cellulose low cost adsorbent (saw dust)</td>
<td>Cd(II), Cr(III) and Ni(II)</td>
<td>The strength sulphuric acid fluxed with (CA) have a profound affection adsorption capacity.</td>
<td>Daiyan et al., 1995</td>
</tr>
<tr>
<td>Adsorption on poly (ethylene terephalate fibers)</td>
<td>Cu(II), Co(II) and Fe(III)</td>
<td>Intake on metal followed in order of Co(II) &gt; Cu(II) &gt; Fe(III). 1 h was sufficient to reach adsorption equil for all the ions. The rate of adsorption decreased with increase in temp.</td>
<td>Yigitoglu et al., 1998</td>
</tr>
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<tr>
<td>Adsorption on sawdust carbon</td>
<td>Cr(VI)</td>
<td>With an initial concn. of 100 mgL⁻¹ at 60°C and pH 2.5 the max. removal was 49.8 mgL⁻¹. Treatment of the exhausted C with 0.1M NaOH removed 87.2% of the adsorbed Cr.</td>
<td>Raji et al., 1997</td>
</tr>
<tr>
<td>Adsorption on copper impregnated sawdust carbon</td>
<td>As(III)</td>
<td>As³⁺ uptake increased from 1.5% to 74% when pH increased from 1 to 12 at 30° and 100 mgL⁻¹ concn. The spent adsorbent can be regenerated using 15% H₂O₂ in 0.2M HNO₃.</td>
<td>Raji et al., 1998</td>
</tr>
<tr>
<td>Adsorption by Shell (oyster)</td>
<td>Cd, Cu, Fe, Mn, Pb and Zn</td>
<td>Preference adsorption for heavy metals is in order of Mn&gt; Z&gt; Fe &gt; Cd &gt; Cu &gt; Pb.</td>
<td>Lee et al., 1997</td>
</tr>
<tr>
<td>Biosorption on Cladophora sp.</td>
<td>Cu(II)</td>
<td>Packed bed column with a flow rate of 1.12 mL⁻¹ min was the optimum condition for removal.</td>
<td>Aksu et al., 1998</td>
</tr>
<tr>
<td>Biosorption by Saccharomyces cerevisiae</td>
<td>Cr</td>
<td>Max. Cr uptake capacity increases with increase in initial Cr conc.</td>
<td>Alemzadeh et al., 1997</td>
</tr>
<tr>
<td>Adsorption on activated carbon fibers</td>
<td>Cr(VI)</td>
<td>Equil. was attained in 1 h. ACFS could remove max. 98% of Cr(VI) from an aq. soln. of 0.75x10⁻³ - 10⁻² molar concn. pH also play significant role for adsorption.</td>
<td>Jung et al., 1997</td>
</tr>
<tr>
<td>Biosorption by acorn cups</td>
<td>Pb²⁺, Cd²⁺, Cr³⁺, Zn²⁺, Mn²⁺, and Fe²⁺</td>
<td>At pH 5.5-8.5, the removal efficiency for different metal was 80.6, 92.2, 85.3, 91.4, 85.0 and 86.0% resp.</td>
<td>Li et al., 1997</td>
</tr>
<tr>
<td>Adsorption by sugarbeat pulp</td>
<td>Ca²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺</td>
<td>In presence of 0.1M NaNO₃ the max. amt. of metal cation uptake was very rapid.</td>
<td>Dronnet et al., 1997</td>
</tr>
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<tr>
<td>Adsorption by waste fly ash</td>
<td>Cr(III)</td>
<td>Flyash treated with NaOH, HCl, EDTA and NaOH/NH₄HCO₃ found to be effective for metal removal.</td>
<td>Sarbak et al., 1998</td>
</tr>
<tr>
<td>Biosorption on Chitosan (CHT)</td>
<td>Cr(VI)</td>
<td>The optimum condition for removal was as follows. pH 3-4, Equil. time 10-12 h. The concn. was &lt;60 mgL⁻¹, SO₄²⁻ interface in the adsorption.</td>
<td>Fu et al., 1997</td>
</tr>
<tr>
<td>Adsorption by biomass of Medicago sativa (alfalfa)</td>
<td>Cd, Cr, Pb and Zn</td>
<td>Optimum pH for metal binding is ~5.0. Equil. reach with 5 min. Binding capacity bound per g of biomass 7.4 mg Cd(II), 7.7 mg Cr(III), 43 mg Pb(II), 4.9 mg Zn(II). However no binding occurred for Cr(VI). Nearly all metal recovered with 0.1 M HCl in column method.</td>
<td>Gardea-Torresday et al., 1998</td>
</tr>
<tr>
<td>Adsorption on fly-ash</td>
<td>Cu, Pb and Zn</td>
<td>Equil. was attained in 4 h.</td>
<td>Gupta et al., 1998</td>
</tr>
<tr>
<td>Sorption on Fe(III)-doped alginitated</td>
<td>As, Se, Cr(VI)</td>
<td>Prove to be efficient adsorbent for metal removal.</td>
<td>Min et al., 1998</td>
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<td>Adsorption on coal fly ash</td>
<td>Pb(II)</td>
<td>Adsorption follows 1st order rate expression.</td>
<td>De et al., 1997</td>
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<td>Sorption on acid-sandy soils</td>
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<td>Optimum pH removal is 3.6-4.3.</td>
<td>Wilkins et al., 1998</td>
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<td>Adsorption on natural zeolite</td>
<td>Pb²⁺, Zn²⁺, Cd²⁺ and Hg²⁺</td>
<td>Pb²⁺ is strongly adsorbed on to modernise but Zn²⁺ and Cd²⁺ are slightly adsorbed</td>
<td>Martinez et al., 1997</td>
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<td>Adsorption on magadiite</td>
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<td>Removal % of metal carbons at equil. increases with increasing temp., and follows the order of Cd(II) &gt; Cu(II) &gt; Zn(II).</td>
<td>Jeong et al 1998</td>
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<td>Adsorption by amorphous SiO₂</td>
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<td>Electron beam irradiation in the presence of sodium formate was improved by addition of amorphous SiO₂.</td>
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<td>Adsorption on coconut shell</td>
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<td>Living cells removed (91-99%) metal ions than inactivated biomass (&lt;50%).</td>
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<td>Sorption by depectinated sugarbeet pulp</td>
<td>Cr(VI)</td>
<td>Optimum contact time was 60 min for an initial conc. of 10 mg Cr⁶⁺ at 20 g L⁻¹ adsorbent dose. Max. removal (55%) was observed at pH 3.3 at 40°C. Desorption was quiet low in acidic and neutral media.</td>
<td>Ozer et al. 1997</td>
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<tr>
<td>Adsorption on Drumstick gum dust</td>
<td>Cr(VI)</td>
<td>At optimum pH, contact time, adsorbent amt., conc. and temp. complete removal is possible. Adsorption capacity decreased in presence of CN⁻ ion.</td>
<td>Samantaroy et al. 1998</td>
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<td>Adsorption on hematite</td>
<td>Cu(II)</td>
<td>Max. adsorption of Cu(II) from aq. soln. takes place at pH 8.0.</td>
<td>Chakravarty et al. 1998</td>
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<td>Biosorption by marine diatom</td>
<td>Cd(II)</td>
<td>The accumulation of Cd EC50 to P. tricornutum was 22.39 mgL⁻¹ after a day of exposure.</td>
<td>Torres et al. 1998</td>
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<tr>
<td>Biosorption on industrial biomass</td>
<td>Fe, Ni, cr, Ca</td>
<td>The max. metal uptake was found to be dependent on soln. pH 4-5 for Fe, 4-7 for Ca, 6-7 for Ni, and 6 for Cr. Adsorption densities are in order of Ca &gt; Cr(III) &gt; Ni &gt; Fe &gt; Cr(VI)</td>
<td>Sekhar et al., 1998</td>
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<tr>
<td>Adsorption on hematite</td>
<td>Cd(II)</td>
<td>The max. removal was found to be 98% for the cadmium conc. 44-88 μmolL⁻¹ at a temp. of 20°C and pH 9.2 with 40 gL⁻¹ of hematite of particle size &lt;200 μm with agitation time 125 rpm rate after 2 h.</td>
<td>Singh et al., 1998</td>
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<td>Sorption on blast furnace</td>
<td>Heavy metals</td>
<td>Effective adsorbent for metal removal.</td>
<td>Lopez et al., 1998</td>
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<td>Adsorption on photofilm waste</td>
<td>Pb(II)</td>
<td>The % adsorption increased from 24 to 82% with an increase in pH from 3.5 to 6.0. Desorption studies showed that 72% of Pb(II) can be adsorbed from the adsorbent at pH 3.0.</td>
<td>Selvaraj et al., 1997</td>
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<td>Biosorption by sea weed</td>
<td>Cr(III), Cr(VI)</td>
<td>Max. metal bound by biomass was 40 mg/g of Cr(III) by ion exchange at pH 4. 70% of Cr(VI) bound to seaweed at pH 2 can be desorbed with 0.2 M H₂SO₄ via redn. to Cr(III)</td>
<td>Kratochvil et al., 1998</td>
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<tr>
<td>Adsorption by lettuce</td>
<td>Cd, Cu, Mn, Ni and Zn</td>
<td>Heavy metals can be effectively removed when they are present at a conc. of 10 mgL⁻¹ or less.</td>
<td>Selvapathy et al., 1998</td>
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<td>Adsorption on blast furnace slag</td>
<td>Pb²⁺, Zn²⁺, Cd²⁺, Cu²⁺ and Cr³⁺</td>
<td>Blast furnace sludge was found to be an effective sorbent for Pb, Zn, Cd, Cu and Cr removal.</td>
<td>Lopez et al., 1998</td>
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<td>Sorption on Sago waste</td>
<td>Pb(II), Cu(II)</td>
<td>The most effective pH range was 4-5.5 for both metals. The sago waste has a greater capacity for Pb (46.6 mgg⁻¹) than for Cu (12.4 mgg⁻¹).</td>
<td>Quek et al., 1998</td>
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<td>Adsorption on activated carbon of hazelnut shell</td>
<td>Cr(III)</td>
<td>Adsorption was max. at 25° with typical waste water contg. 30 mg Cr³⁺L⁻¹.</td>
<td>Ekinci et al., 1997</td>
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<td>Adsorption on carbon</td>
<td>Cr(III), Cr(VI), Pb(II), Zn(II)</td>
<td>Carbon adsorbent selectively removed the anions of hexavalent chromium.</td>
<td>Lalvani et al., 1998</td>
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<td>Adsorption on Australian flyash</td>
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<td>Adsorption capacity increased as metal initial conc. decreases.</td>
<td>Ayala et al., 1998</td>
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<td>The equil. capacity and initial sorption rate with the effect of initial Pb²⁺ conc. and peat particle size and temp. was evaluated.</td>
<td>Ho et al., 1998</td>
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<td>Adsorption on carbonized wood powder</td>
<td>Hg(II)</td>
<td>Wood powder carbonized at 1000°C achieved the best removal of heavy metals among the wood based materials.</td>
<td>Pulido et al., 1998</td>
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<td>Sorption on formaldehyde cross linked saccharomyces cerevisiae</td>
<td>Cr(VI)</td>
<td>The Cr uptake at 60% soln. of the biomass was 6.3 mgg⁻¹ at an optimum pH of 2.5. Desorption was achieved particularly with combined soln. of 1% (w/v) formaldehyde and 1M HNO₃</td>
<td>Zhao et al., 1998</td>
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<tr>
<td>Adsorption on different types of MnO₂</td>
<td>As(III)</td>
<td>MnO₂ possess strong adsorbing properties to As(III).</td>
<td>Chen et al., 1998</td>
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<td>Adsorption by Maifanshi</td>
<td>Pb$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$</td>
<td>Maifanshi has been found effective adsorbent for removal of heavy metals. pH is a main factor controlling the adsorption.</td>
<td>Gao et al., 1997</td>
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<td>Biosorption by microalgae</td>
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<td>Proved to be effective for metal removal.</td>
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<td>Max. sorption (71.6%) was at pH 6.5.</td>
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<td>Adsorption on coconut fiber pith-based pseudo activated carbon</td>
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<td>Manju et al., 1997</td>
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<td>Cr$^{3+}$,Cr$^{6+}$, Pb$^{2+}$ and Zn$^{2+}$</td>
<td>As adsorbent selectively removed only the dichromate anions from solns. (It has no affinity for Cr, Zn and Pb cations esp. at low pH).</td>
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<td>Adsorption on low cost adsorbent</td>
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<td>Adsorption on calcium humate</td>
<td>Ni, Cu, Cd, Hg, Pb</td>
<td>The adsorption capacity of Ca humates for different metal ions increased with increasing mol. wt. (i.e., Ni &lt; Cu &lt; Cd &lt; Hg &lt; Pb).</td>
<td>Vodicka et al., 1997</td>
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<td>Adsorption on photofilm waste</td>
<td>Ni(II)</td>
<td>The percent adsorption increased from 41 to 96 with increase in pH from 3.5 to 7.0. 86% of Ni(II) can be desorbed at pH 3.5.</td>
<td>Selvaraj et al., 1998</td>
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<td>Biosorption on filamentous fungi</td>
<td>Ni(II)</td>
<td>Nickel accumulation by selected strains is fast occurring in less than 30 min.</td>
<td>Mogollon et al., 1998</td>
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<td>Adsorption on peat</td>
<td>Cu, Cd, Co, Ni and Zn</td>
<td>The sorption capacities are as follows: Cd (99.47 μmolg⁻¹), peat (11.18 mgL⁻¹). 446.94 μmolg⁻¹, cobalt 26.34 mgL⁻¹, peat, copper (198.31 μmolg⁻¹), (12.60 mgL⁻¹), peat, nickel (113.34 μmolg⁻¹) (6.65 mgg⁻¹) peat.</td>
<td>Mckay et al., 1998</td>
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<td>Biosorption on bagass xanthates (Bx)</td>
<td>Ni(II)</td>
<td>Highly efficient for nickel removal. The residual concn. of Ni after treatment can be reduced to 0.01 mgL⁻¹.</td>
<td>Changgeng et al., 1996</td>
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<td>Biosorption on pretreated biomass</td>
<td>Cd(II)</td>
<td>At soln. pH of 5, the max. adsorption capacity of the pre-treated biomass is 1.1 mmolg⁻¹; 90% adsorption takes place within 30 min.</td>
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<td>Adsorption with activated calcium phosphate</td>
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<td>Removal reached 98% under optimum condition.</td>
<td>Cao et al., 1998</td>
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<td>Adsorption by organic waste materials</td>
<td>Cr(III)</td>
<td>Barks from deciduous species have highly affinity for Cr(III).</td>
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<td>Adsorption by apple residues</td>
<td>Cu(II), Pb(II), Cd(II)</td>
<td>AR as well PAR showed higher selectivity for Pb ions than Cu and Cd ions.</td>
<td>Lee et al., 1998</td>
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<td>Adsorption on bentonite</td>
<td>Cr(III)</td>
<td>Complete recovery was possible with 20 ml of effluent with 7.5 g of bentonite.</td>
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<td>Pb²⁺, Hg²⁺ and Cd²⁺</td>
<td>Sorbent is effective for quant removal of metal ions at pH 6.0.</td>
<td>Subha et al., 1998</td>
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<td>Adsorption on crab shell particles</td>
<td>Pb(II)</td>
<td>Approx. 99% of the lead was removed within 2 h after contact with crab shell. When crab shell dose increased from 0.5 to 1.5 gL⁻¹ 84%, removal efficiency improved to 99.8% at pH 2.0.</td>
<td>Lee et al., 1998</td>
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<td>Adsorption by fly ash</td>
<td>Cr(III)</td>
<td>Results indicated a decrease in initial Cr conc. in the waste water from 150 to 0.008 ppm.</td>
<td>Pavas et al., 1998</td>
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<td>Adsorption on activated carbon</td>
<td>Heavy metals</td>
<td>Effect of pH and temp. is main factor for adsorption.</td>
<td>Cotoruelo et al., 1998</td>
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<td>Adsorption on magnetite</td>
<td>Pb(II), Cd(II)</td>
<td>The adsorption was significant even at low pH of the initial soln. i.e., in presence of positive charge surface. Affinity for Cd(II) is 4 times greater than Pb(II).</td>
<td>Georgeaud et al., 1998</td>
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<td>Adsorption on activated carbon</td>
<td>Cr(VI)</td>
<td>Was efficient for Cr(VI) removal.</td>
<td>Nagaev et al., 1998</td>
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<td>Adsorption on rice hush</td>
<td>Pb(II)</td>
<td>Max. adsorption was obsd. with 0.01 mol dm⁻³ acid solution (HNO₃, HCl, H₂SO₄ and GCIO₄) using 1000 mg of adsorbent for 4.82x10⁻⁵ mol dm⁻³ lead conc. is less than 10 min equil. time.</td>
<td>Khalid et al., 1998</td>
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<td>Adsorption on poly-acrylamide-grafted sawdust</td>
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<td>Biosorption by immobilized biomass of Rhizopus arrhizus</td>
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<td>Biosorption by white rot fungi</td>
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<td>Biosorption by magnetite immobilized cell of Pseudomonas putida</td>
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<td>Dil. HCl prepared magnetite immobilized cell of P. putida 5-x had higher biosorption capacity than fresh P. putida cells. The removal and recovery rates of biosorption were 96 and 95% resp. Recovery is possible with 0.6N HCl.</td>
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<td>Lime enhanced the ability of removal at low initial Zn(II) conc. Whereas no significant effect is seen at higher initial Zn(II) concentration.</td>
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<td>Removal of cadmium (in a range of 8 days) varied from 86% to 96%.</td>
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<td>Adsorption on Fe(III)/Cr(III) hydroxide</td>
<td>Cu(II)</td>
<td>Quant. removal of Cu(II) by 50 mg/50 ml adsorbent was obsd. at pH 5.0 for a Cu(II) conc. of 40 mgL⁻¹, Desorption of Cu(II) from Cu(II) loaded adsorbent was 55.4% at pH 3.0.</td>
<td>Namasivayam et al., 1999</td>
</tr>
<tr>
<td>Adsorption on China clay</td>
<td>Cd(II)</td>
<td>Presents a new modelling technique for removal.</td>
<td>Chakravarty et al., 1997</td>
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<tr>
<td>Adsorption on buckwheat</td>
<td>Heavy metals</td>
<td>The alk. extractions of buckwheat shell has been detd. as efficient adsorbent for heavy metals removal.</td>
<td>Shekurov et al., 1998</td>
</tr>
<tr>
<td>adsorption on Iron Rich Material (IRM)</td>
<td>Cr(VI)</td>
<td>Proved to be effective for Cr(VI) removal.</td>
<td>Sengupta et al., 1998</td>
</tr>
<tr>
<td>Adsorption on poly (acrylic acid)</td>
<td>Cr</td>
<td>Cr retention was found to increase with pH. Desorption of Cr is possible under acidic condition.</td>
<td>Heitz et al., 1999</td>
</tr>
<tr>
<td>Adsorption on various type of activated carbon</td>
<td>Cr(VI)</td>
<td>The optimum pH for removal of total chromium was 2 for wood based activated carbon, while for coconut shell and duscoal the optimum pH was around 3-4.</td>
<td>Selomulye et al., 1999</td>
</tr>
<tr>
<td>Adsorption on wood powder carbonized at high temp.</td>
<td>Hg(II)</td>
<td>The carbonized temp. that provide wood powder with high removal capacity ranged from 600° to 1400°C.</td>
<td>Pulido et al., 1998</td>
</tr>
<tr>
<td>Adsorption on activated from Sterculia foetida L. fruit shell</td>
<td>Cu(II)</td>
<td>SFFG acts as better adsorbent than acid/or water treated one Equal time is independent of concn. of Cu(II) treatment of C and the temp. of the soln.</td>
<td>Sreenivasulu et al., 1998</td>
</tr>
<tr>
<td>Adsorption on photofilm water waste</td>
<td>Cr(VI)</td>
<td>Maximum removal of 95% was recorded at 10 mgL⁻¹ Cr(VI). Desorption studies show that 92% Cr(VI) can be desorbed at pH 12.0.</td>
<td>Selvaraj et al., 1998</td>
</tr>
<tr>
<td>Adsorption on activated carbon</td>
<td>Cr(VI)</td>
<td>Carbon exposed over sand particles is proposed to be important mixed adsorbent for adsorption.</td>
<td>Bandyopadhyay et al., 1998</td>
</tr>
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<tr>
<td>Adsorption on different adsorbent (i.e., Kendu fruit gum dust, DGD, Drumstick gum dust (DGD), green peas skin dust (GPSD))</td>
<td>Cr(VI)</td>
<td>96% removal of Cr(VI) was possible with KGD, DGD, GPSD</td>
<td>Samantaroy et al., 1998</td>
</tr>
<tr>
<td>Adsorption by polymers</td>
<td>Hg(II)</td>
<td>&gt;90% of the Hg may be removed with 0.13 mL⁻¹ adsorbent</td>
<td>Pederson et al., 1999</td>
</tr>
<tr>
<td>Adsorption on natural zeolite</td>
<td>Pb, Cu, Cd, Zn</td>
<td>Preference sequence of adsorption was Pb&gt;Cu&gt;Cd&gt;Zn for modernite, and Pb&gt;Cu&gt;Zn&gt;Cd for clinoptilolite.</td>
<td>Yuan et al., 1999</td>
</tr>
<tr>
<td>Biosorption by pre-treated biomass</td>
<td>Pb(II), Cu(II)</td>
<td>Effective adsorbent for removal of both metals.</td>
<td>Matheickal et al., 1999</td>
</tr>
<tr>
<td>Adsorption on Japanese red pipes</td>
<td>Cr(VI)</td>
<td>Cr⁶⁺ was effectively adsorbed at pH 2-3. The adsorption rate was 95% and the amt. adsorbed Cr⁶⁺ was 4.72 mgg⁻¹.</td>
<td>Aoyama et al., 1999</td>
</tr>
<tr>
<td>Biosorption by Pergilus niger</td>
<td>As, Pb, Cd, Cu and Ni</td>
<td>Pretreated biomass by boiling in 0.1N NaOH sol. for 15 min. exhibited higher Pb, Cd and Cu removal capacity than live biomass. Biosorbed metal ions were effectively eluted with 0.05N HNO₃ soln.</td>
<td>Kapoor et al., 1999</td>
</tr>
<tr>
<td>Biosorption by industrial biomass</td>
<td>Zn, Cu and Ni</td>
<td>Most effective pH for removal was pH (3-11.5)</td>
<td>Zoumboulis et al., 1999</td>
</tr>
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<tr>
<td>Adsorption on quaternized rice hulls</td>
<td>Cr(VI)</td>
<td>An increase in column bed depth resulted in a longer service time at CL/CO = 0.5 breakthrough. The presence of SO₄²⁻ interfered with the sorption process. Cr(VI) could be recovered quant. by eluting with 0.5M NaOH soln.</td>
<td>Low et al., 1999</td>
</tr>
<tr>
<td>Adsorption on polymer</td>
<td>Hg(II)</td>
<td>Each polymer removed 74.9-88.4% of the Hg. The estd. optimal conc. of the 2 polymers is ~2.33 mL of each/L of the waste and &gt;90% of the Hg may be removed with 0.13 mL/L.</td>
<td>Pederson et al., 1999</td>
</tr>
<tr>
<td>Biosorption on mycelial waste</td>
<td>Cd(II), Pb(II)</td>
<td>Equal sorption isotherms of Cd(II) and Pb(II) follow the typical Langmuir adsorption model.</td>
<td>Stoica et al., 1999</td>
</tr>
<tr>
<td>Biosorption by dry biomass of Sargassum polycystum</td>
<td>Cd(II)</td>
<td>The biomass which were dried at 80°C has Cd uptake capacity of 71.39 mg Cdg⁻¹ biomass at pH 4.6 and 70.66 mg Cdg⁻¹ biomass at pH 5.6.</td>
<td>Srikrajib et al., 1999</td>
</tr>
<tr>
<td>Adsorption on activated carbon</td>
<td>Cr(VI), Pb(II), Ni(II)</td>
<td>The adsorption was in the order of Cr(VI) &gt; Pb(II) &gt; Ni(II). Max. adsorption of Cr(VI) occurred near pH 3-4, while that of Pb(II) and Ni(II) was near pH 11 and 12.</td>
<td>Park et al., 1999</td>
</tr>
<tr>
<td>Adsorption on biogas residual</td>
<td>Cr(III)</td>
<td>For a 10 mgL⁻¹ Cr(III) concn. a max. removal of 85% by 4 gL⁻¹ adsorbent was obtained at an initial pH &gt; 3.0.</td>
<td>Namasivayam et al., 1999</td>
</tr>
<tr>
<td>Adsorption on Hydrotalcite</td>
<td>Cr(VI)</td>
<td>The extent of adsor. decreased from 23.2 mg to 4.9 mg with increase in pH from 2.0 to 10.0. About 95.7% of Cr(VI) can be desorbed from the adsorbent with 0.1M NaOH.</td>
<td>Manju et al., 1999</td>
</tr>
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<tr>
<td>Adsorption on coniferous leaves</td>
<td>Cr(VI)</td>
<td>P. densiflora leaves were selected to study optimum operation condition for treatment of waste water contg. Cr(VI). The adsorption data were well fitted to the Freundlich isotherm.</td>
<td>Aoyama et al., 1999</td>
</tr>
<tr>
<td>Adsorption on fly ash and flyash/lime</td>
<td>Cu(II), Zn(II) and Pb(II)</td>
<td>The higher removal effectiveness was achieved by using 100 gL⁻¹ of adsorbent with 20% mass of lime at pH 5.</td>
<td>Ricou et al., 1999</td>
</tr>
<tr>
<td>Adsorption by coconut husk</td>
<td>Hg(II)</td>
<td>A max. of 99.4% with 2g of sorbentL⁻¹ was obsd. at 125 μ mol Hg(II)L⁻¹ conc. at pH 6.0.</td>
<td>Sreedhar et al., 2000</td>
</tr>
<tr>
<td>Adsorption by lignin</td>
<td>Cr(VI)</td>
<td>Removal upto 63% Cr⁴⁺ and 100% Cr²⁺ from aq. solns.</td>
<td>Lalvani et al., 2000</td>
</tr>
<tr>
<td>Sorption on natural zeolite rich in Clinoptilolite</td>
<td>Cd(II), Ni(II)</td>
<td>Removal capacity was higher for Cd²⁺ cations than for Ni²⁺ cations.</td>
<td>Martinez et al., 1999</td>
</tr>
<tr>
<td>Adsorption by recycled iron material</td>
<td>Pb(II)</td>
<td>An influent Pb concn. and pH 10 ppm and 5.5 resp. A empty bed contact time of &gt;2.5 min provides for efficient use of the adsorbent and yields a solid phase loading capacity of ~40 mgg⁻¹.</td>
<td>Smith et al., 2000</td>
</tr>
<tr>
<td>Adsorption by rice husks</td>
<td>Hg(II)</td>
<td>Max. adsorption was obsd. at 0.01 mol/dm³ acid solution (HNO₃, HCl, H₂SO₄, HClO₄).</td>
<td>Khalid et al., 1999</td>
</tr>
<tr>
<td>Sorption at the oak ridge Y-12 plant</td>
<td>Hg(II)</td>
<td>SIR 200, Kenyle; X and GT73 (Rohni and Haas) were the best material for Hg removal.</td>
<td>Hollerman et al., 1999</td>
</tr>
</tbody>
</table>
Table 1.4B A Selective Summary of Recent Work Done on Treatment of Water and Wastewater Containing Organic Compounds.

<table>
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<tr>
<td>Adsorption on macro-porous resin</td>
<td>Monophenols</td>
<td>GDX-502 was excellent sorbent. The aq. concn. recovery for phenols was 93.7% excepting 2,4-dinitrophenol.</td>
<td>Bao et al., 1998</td>
</tr>
<tr>
<td>Extraction with solid phase disk and HPLC analysis</td>
<td>Herbicides</td>
<td>The HPLC analysis was carried out with uv/vis detector.</td>
<td>Guidotti et al., 1997</td>
</tr>
<tr>
<td>Adsorption on C₁₅ speed disks (Baker bond)</td>
<td>Polychlorinated dibenzo-p-dioxins and dibenzofuran</td>
<td>The disk is designed for analysis of organic compound in water with high level of particulate matter but no analysis of PCDD/PCDF.</td>
<td>Pujadas et al., 1999</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Organic matter</td>
<td>Ion exchange resin was very promising.</td>
<td>Heijman et al., 1999</td>
</tr>
<tr>
<td>Adsorption on natural sediments</td>
<td>Chlorinated benzene</td>
<td>Promising sorbent for the removal of chlorinated benzene.</td>
<td>Chen et al., 2000</td>
</tr>
<tr>
<td>Adsorption on silica gel</td>
<td>Organochlorine pesticides</td>
<td>The recovery of PCBs as PCB 25 were 97-118%.</td>
<td>Kang et al., 1999</td>
</tr>
<tr>
<td>Adsorption on bagasse</td>
<td>Congo red</td>
<td>The operating variables were dye concn. adsorbent dosage and contact time.</td>
<td>Kavitha et al., 1999</td>
</tr>
<tr>
<td>Biosorption by Pseudomonas putida</td>
<td>2,4-dinitrophenol</td>
<td>Batch expts. showed a rapid decrease in pollutant concn. and the superiority of activated carbon to the other carriers</td>
<td>Kosseva et al., 1999</td>
</tr>
<tr>
<td>Adsorption on Hg electrodes</td>
<td>Aniline</td>
<td>The dye can be adsorbed on Hg electrodes to give a well defined redn. polorg.</td>
<td>Zhang et al., 1999</td>
</tr>
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<tr>
<td>Adsorption on PVC lysimeter</td>
<td>Pesticides (alachlor, atrazine, isofenphos, triadimeton)</td>
<td>Only isofenphos demonstrated straight adsorption 9%.</td>
<td>Koskinen et al., 1999</td>
</tr>
<tr>
<td>Filteration</td>
<td>Total hydrocarbon</td>
<td>Clarify is capable of consistently removing &gt;95% of total hydrocarbon.</td>
<td>Hayns et al., 1998</td>
</tr>
<tr>
<td>Determination by Reverse phase HPLC</td>
<td>Aldehyde</td>
<td>pH 3.0 of citrate buffer soln, 40° of reaction temp. 15 min of reaction time and 0.012% of DNPH conc. were chosen optimum condition.</td>
<td>Choi et al., 1999</td>
</tr>
<tr>
<td>Adsorption on octa-decyl bonded silica membrane</td>
<td>Polychlorinated biphenyls</td>
<td>The detn. of biphenyl, polychlorinated biphenyls and Aralors adsorbed was performed phosphorimetry.</td>
<td>Arruda et al., 1999</td>
</tr>
<tr>
<td>Solid-phase extraction by GC/MS</td>
<td>Organochlorine pesticides</td>
<td>47 mm SDB-XC bond disk GC/MS was used for analysis.</td>
<td>Fujimoto et al., 1999</td>
</tr>
<tr>
<td>Adsorption by sediments</td>
<td>Hydrophobic org. compd.</td>
<td>Appreciable amount of removal was achieved.</td>
<td>Chen et al., 1999</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Pentachlorophenol</td>
<td>PCP was rapidly biodegradable after an adaptation period of 10-20 days.</td>
<td>Ingersler et al., 1998</td>
</tr>
<tr>
<td>Sorption in aquifer material</td>
<td>Syndrophobic org. pollutant</td>
<td>Review of 89 ref. on sorption in ground water and soil.</td>
<td>Grathwoi et al., 1997</td>
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<tr>
<td>Biological filtration</td>
<td>Amino acids, biodegradable organic carbon and chlorine</td>
<td>Achieved a removal of 46% of TDAAS and a removal of 24% of BDOC.</td>
<td>Prevost et al., 1998</td>
</tr>
<tr>
<td>Biosorption</td>
<td>Long chain fatty acids</td>
<td>Batch expt. were conducted for characterization of the biosorption.</td>
<td>Hwu et al., 1998</td>
</tr>
<tr>
<td>Biodegradation by Phanerochaete</td>
<td>Congo red</td>
<td>This fungus readily degraded upto 718 um (500 mgL⁻¹) congo Red in 2.0% matt agar.</td>
<td>Tatarko et al., 1998</td>
</tr>
<tr>
<td>Removal by denitrification</td>
<td>Organic pollutants and nitrate</td>
<td>Denitrified with removal of 90%-93% of the COD of the whey powder.</td>
<td>Zayed et al., 1998</td>
</tr>
<tr>
<td>Composting</td>
<td>Polycyclic aromatic hydrocarbon</td>
<td>Result indicate that most biodegradation occurred in the active composting phase.</td>
<td>Joyce et al., 1998</td>
</tr>
<tr>
<td>Reductive dechlorination</td>
<td>Polychlorinated biphenyls</td>
<td>During first 4 month, dechlorination reduced the aq. total chlorine from 3.2 to 2.5 per biphenyl.</td>
<td>Sokol et al., 1998</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Matalachlor herbicides</td>
<td>Degradation of the herbicides metolachlor was used as model compd.</td>
<td>Kontchou et al., 1998</td>
</tr>
<tr>
<td>Removal with a fluidized bed bioreactor</td>
<td>Trichloroethene</td>
<td>A phenol to trichloroethene mass ratio of 75:1 gave an av. 60% removal of 0.1 mg trichloroetheneL⁻¹ at empty bed contact time of 3 min.</td>
<td>Seger et al., 1997</td>
</tr>
<tr>
<td>Adsorption by chitin</td>
<td>Basic dye</td>
<td>Batch kinetic study involving the adsorbent concn temp and pH have been investigated.</td>
<td>Annadurai et al., 1996</td>
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<tr>
<td>Biodegradation by Halobacteria</td>
<td>Organophosphorus</td>
<td>Puerto Rico (PR # 3 and PR # 5) were evaluated to assess their potential to degrade 2 com. parathion and paraoxon.</td>
<td>Quinones et al., 1998</td>
</tr>
<tr>
<td>Adsorption on peat</td>
<td>Pesticides</td>
<td>Batch sorption of pesticides onto an org. sorbent (e.g. peat), followed by sepn. (filtration) and finally degradation.</td>
<td>Mullin et al., 1998</td>
</tr>
<tr>
<td>Biosorption on dried activated sludge</td>
<td>Monophenols and monophenols</td>
<td>The max. loading capacity of biosorbent was 86.1 mgg^{-1} for phenol, 102.4 mgg^{-1} for o-chlorophenol and 116.3 mgg^{-1} for p-chlorophenol at 100 mgL^{-1} initial pollutant concn.</td>
<td>Aksu et al., 1998</td>
</tr>
<tr>
<td>Treatment using WO₃ as substrate complex photocatalyst</td>
<td>Wastewater from printing and dying</td>
<td>The satisfying results can be achieved under the condition of the optimal catalyst.</td>
<td>Nan et al., 1998</td>
</tr>
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</table>

Contd.
REFERENCES


Anon, River Pollution Commission, Fifth Report of the Commissioner Appointed in 1968 to enquire into the best means of preventing the pollution of rivers

Aoyama, Masakazu; Sngiyama, Tomoaki, Seiki, Kazuto, Tsuda, Maynmi; Cho. Nam Seok Rinson Shikenjoho (Hokroido) 1999, 13(2), 15-19 (Japan).


Arnfalk, P.; Wasay, S. A. ; Tokunage, S., Water Air Soil Pollut. 1996, 87(1-4), 131-48 (Eng)


Bennett, J.R.; *Metal Finish. J.* 1972, 18, 212, 272-76.


Burinskii, S.V.: Khim Volokna 1996, (6), 16-19 (Russ.).

Bunnskii, S.V.: Khim Volokna 1996, (6), 16-19 (Russ.).


Cao, Wei, Huang Shaode; Hu, Jiashan, Han, Zhonghna, Zhang XiaoL Shandong Jiancai Xueyuan Xuebao 1998, 12(2), 166-167, 171 (Ch), Shandong Jian Cai Xueyuan Xuebao Bianjibu.


Changgeng, Zhong; Donggong, Tang; Qiayun, Chen Chin.; J. React Polym. 1996, 5 (1-2), 57-63 (Eng.)


Chen, Hong.; Ye, Zhaojie.; Fang, Shi.; Lin, Xun Xiang.; Zhongguo Huanjing Kexue 1998, 18(2), 126-130 (Ch).


Chui, V.W.D.; Mok, K.W.; Ng, C.Y.; Luong, B.P.; Ma, K.K., Environ. Int. 1996, 22 (4), 463-468 (Eng).


Crowle, V.; Metal Finishing J. 1971, 17, 51-54.


Dikshit, V.P.; Agarwal, I.C.; Shukla, N.P.; Asian Environ. 1990, 12 (1) 64-72.


Donnelly R G.; Goldsmith, R. L.; McNulty, K.J.; Tan, M. Plating. 1974, 61 5. 432-42


Gao, Xiaohong.; Rong, Qiutao.; Huanjing Wuran Yu Fangzhi 1997, 19 (4), 4-7 (Ch).


Georgeaud, V.M.; Ambrosi, J.P.; Bottero, J.Y.; Rochette, P. Mineral. Mag. 1998, 62A (Pt-1), 513-514 (Eng), Mineralogical Society


Golomb, A., Plating, 1972, 59 316.


Hayns, Andrew B.; Guellett, Paul.; Int. J. Hydrocarbon Eng. 1998, 3(2), 74-76. 78

He, Dexiang; Liao, Liewen; Xu, Ruixuan.; Faming Zhuanli Shenqing Gongkai Schuomingshu 1989, CN 1, 033, 976, 19th July, 6 pp.


Hu, Yanhai; Wang, Jiku.; Shao, Shuhua.; Wujiyan Gongye 1997, (2), 5-6 (Ch).

Huang, Bi.; Wu, Xinhua.; Huang, Bizhong.; Huanjing Kexue Jinzhan 1998, 6 (1), 77-81 (Ch).


Isaza, Adsiana Echavarria; Casafus, Monica Moreno; Ochoa, Claudia Ramirez; Martinez, Claudia Tamayo; Molina, Carlos Saldarriaga. Rev. Colomb Quim 1998, 27(1), 83-88 (Span).


Jackson, D V. Metal Finish J. 1972, 235-42.


Jiang, Ting.; Shi, Yinui.; Hua, Jinyuan., Linchan Huaxue Yu Gongye 1996, 16(2), 49-53 (Ch).


Kang, Yuhui.; Sheng, Guoying.; Fu, Jiamo.; Mai, Bixian Fenxi Huaxue 1999, 27(II), 1258-1263.


Karnaukho, A.I.; Tkachenko, V.M.; Shestidesyatnaya, N.L.; Uskha, USSR.; Pochvovedenic, 1989, 11, 118-23.


Lacy, W.J.; Cywin, A.; Plating, 1968, 55, 1299-1301.


Li, Chunhua.; Lizi Jiaohuan Yu Xifu, 1994, 10(5), 443-6.

Li, Lin.; Feng, Yijuan.; Xie, Jiali.; Shan, Shuxiang Huanjing Gongcheng 1997, 15 (5), 14-16 (Ch).


Mattock, G.; *Metal Finishing J.* 1968, 14, 168-75.


McDeugall, Gloria J.; CHEMSA 1982, 8, 4, 24 -7.


Meng, Qin, *Shuichuli Jishu* 1998, 24(3), 175-178 (Ch), Shuichuli Jishu Bianji Weiyanhmi.


Mu, Guannan; Yang, Chunfen; Wuli Huaxue Xuebao, 1995, 11(2), 157-61.


Nagaev, V.V.; Shulev, M.V.; Sirotkin, A.S.; Khim. Prom-St (Moscow) 1998 (7), 411-414 (Russ.).


Namasivayam, C.; Kadirvelu, K.; *Carbon* 1999, 37(1), 79-84 (Eng.).


Malaysian Rubber Board.


Rachel, C.; *Silent Spring*. 1960, U.S.A.


Ren, Qin.; Zhang, Xiuzhi, Qi.: Mo Kexue Yu Jishu, 1993, 13(4), 1-8.


Saito, Naoto; Aoyama, Masakazu; Rinsan; Shikengocho (Hokkaido). 1991, 5(6), 15-18.


Swanson, C. L.; Civil Engineering, 1971, 41, 49.


Tang, Lanmo.; Shen, Dunyu; Fu, Maiqun.; Huang, Huanli.; Huaxue Shijia 1998, 39(10), 549-552 (Ch), Shanghai Huaxue Huagong Xuehui.


Thompson, J.; Miller, V.J.; Plating, 1971, 58, 809-12.


Tomany, J. P.; 1974, Air Pollution, Emission the Regulation and Control Elsevier, N. Y.


Train, R. E.; Scavenger, 1976, 6, 1.


Voldman, S. G.; Ramyantsev, V. K.; Kulakova, V. V.; Tsvetn. Met., 1989, 12, 46-8


Welz, Berhard.; Xu, Shukun.; Sperling, Michael.; Appl. Spectrosc. 1991, 45(9), 1433-43.

Werner, H. W.; Presented at 27th Ind. Waste Conf. Perdue University, 1972


Wu, Dehuai; Chen, Xiaoxing; Tian, Bingshi; Xu, Chaohao; Huanjing Wuran Yu Fangzhi, 1994, 16(2), 11-15.

Wu, Dunao; Lu, Guofu; Shangai Huanjing Kexue, 1991, 10(8), 20-3.

Wu, Dunao; Lu, Wenyu; Shangai Huanjing Kexue, 1991, 10(2), 19-23.

Wu, Jianming; Gao, Xianbiao; Gao, Bimo; Yang, Gao; Lu, Liping; Guan Lisheng; Turang Xuebao, 1991, 28(4), 452-6.

Wu, Qianjing; Li Xing; Li Fude; Shanghai Huanjing Kexue 1995, 14(12), 10-12 (Ch).

Xie, Jiali; Feng, Yijun; Sichuan Dauxe Xuebao, Ziran Kexueban 1995, 32(5), 577-82 (Ch).

Xie, Yanxia; Hu, Qiosheng; Lizi Jiaohuan Yu Xifu, 1990, 6(4), 281-3.

Xu, Jiangghua; Lu, Yueging; Li, Yimin; Xu, Lithong; Chen, Feng Shuichuli Jishu 1998, 24(6), 359-362 (Ch); Shuichuli Jishu Bianji Weiyuanhui.

Xu, Rong; Tang, Yuezin; Wang, Jianhua; Yang, Hong, Huanjing Kexue 1998, 19(4), 72-75 (Ch) Kexue Chubaashe.

Xu, Yuping; Schwartz, Franklin W; Traina, Samuel J; Environ. Sci. Technol. 1994, 28(8), 1472-80.


Yang, Bohe; Wang, Ping; Dai, Guijun; Youkuangye, 1992, 11(1), 19-22, 18.

Yang, Chunfen; Yang Zhongmin; Mu, Guannan; Huan Jing Huaxue 1994, 13(2), 176-80.

Yang, Huirong; Li, Bina; Li, Hongyin; Lin, Shengshen; Xu Yong; Lai, Yiangle; Guangzhou Huagong 1995, 23(2), 17-22 (Ch)


Youssef, A.M.; Mostafa M.R.; *Indian J. Technol.,* 1992, 30(8), 413-16


Zaoug, C; Sadaoni, Z; Charbit, G.; Charbit, F.; *Recent Prog. Genie Procedes* 1995, 9 (42, Genei des Procedes Complexes), 219-224 (Fr.).


Zhang, Huifu.; Ma Yulli.; *Lizi Jiaohuan Yu Xifu, 1988, 4(6), 449-53

Zhang, Li; Yu, Yueting.; *Lizi Jiaohuan Yu Xifu* 1995, 11(6), 545-549 (Ch).


CHAPTER 2
CHAPTER 2

ADSORPTION STUDIES OF HEAVY METALS ON TECTONA GRANDIS: REMOVAL AND RECOVERY OF Zn(II) FROM ELECTROPLATING WASTES

2.1 INTRODUCTION

The water bodies are polluted by different contaminants like organics, refractories, heavy metal ions etc., from domestic sewage, agricultural and industrial wastewater discharges. Waters containing significant concentrations of some of the metal ions are toxic to human beings, animals as well as aquatic organisms. Therefore efforts in different ways have been made to control water pollution, through easy and economical treatment measures.

Amongst the heavy metals Zinc is chronically and acutely toxic to several aquatic organisms (Barry, T. Hart, 1974). There are many opportunities for contamination of water by Zinc, both from natural sources as well as from industrial uses.

Zinc is generally released through industrial waste discharges from pulp and paper mills, organic chemicals, petrochemicals, and inorganic chemicals, manufacturing factories, fertilizers, petroleum refining units, basic steel works foundries and non ferrous metal works and steam generation power plants etc.

Excessive ingestion of Zinc may affect the human metabolism through the changes brought about in the mineral and the enzyme budget, especially the children and patients already suffering from irregular metabolism (Schroeder, H.A; 1967).
Zinc has been reportedly found toxic to plant growth when present in the range of 0.3 ± 0.1 mgL⁻¹ for Soyabean (Early B.B., 1943), 0.5 mgL⁻¹ for subterranean clover (Alain J. Rubin, 1976), and 0.5 mgL⁻¹ for maize and beans (Gangoli, N. et al., 1973).

In India, the waste water from viscose Rayon factory (Sastry, G.A. et al., 1971) contained Zinc in concentration ranging from 171-210 mgL⁻¹. In Rajasthan at Debary, Zinc smelter release effluents (Bhandari, L.M; 1973) which contained Zinc concentrations upto 160 mgL⁻¹.

The USPHS (United State Public Health Service) recommends that the concentration of Zinc should not exceed 10 mgL⁻¹ both in surface waters and irrigation waters (Alan J. Rubin; 1976). The derived working level for Zinc in irrigation water is 2.0 mgL⁻¹ as recommended by the Australian Water Resources Council (Barry, T. Hart, 1974). Tolerance limit, for industrial effluents containing Zinc, discharged into inland surface waters is 5.0 mgL⁻¹ as suggested by the Indian Standard Institution (Indian Stands Institution, 1974).

It is matter of concern that most of the toxic metals including Zinc could not be removed during traditional processes used in water treatment for public water supplies (Forstner, U, et al., 1979, Funke, J.N.; 1975, Jackson's, et al., 1970; Netzal, A. et al., 1974; Nilsson, R; 1971).

The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from waste water by selecting some adsorbent under optimum operating conditions. The behaviour of some adsorbents like silica gel, pyrolusite, Fe(III) hydroxide, sawdust for the removal and recovery of Hg²⁺, Cr⁶⁺, Ni²⁺, Cu⁺², Cd⁺², Pb⁺², Zn⁺² and
Mg$^{2+}$ from river and industrial waste water have been studied in our laboratory (Ajmal et al., 1989, 1993, 1995, 1996). The adsorption behaviour of Zinc on activated carbon (Sigworth, E.A. et al., 1972) and Flyash (P.V.S. Prabhu et al., 1981) has been studied.

Indian Teak being a deciduous plant, sheds its leaves in the months of March - April. The disposal problem of waste shed leaves can be minimized by utilizing them as adsorbent for the removal of heavy metal ions from waste water.

In this chapter results of laboratory batch studies on the adsorption of Zinc from aqueous solution by Teak leaves are reported. The effect of contact time, pH, temperatures, concentrations and dose on the removal of Zinc(II) by Teak leaves have been studied. The thermodynamic parameters viz. $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$ have been calculated and described.

The adsorption and desorption studies under appropriate conditions have been utilized for the removal and recovery of Zinc(II) from electroplating waste water.

2.2 MATERIAL AND METHODS

2.2.1 Adsorbent:

Sieved leaves of Tectona grandis (Teak leaves) were used as an adsorbent for the removal of Zn(II) from aqueous solution. The leaves were dried, crushed and washed thoroughly with double distilled water to clean the adhering dirt and finally dried in an air oven at 100-105°C for 24 h. After drying the adsorbents was sieved through 150 mesh size and used as such.
2.2.2 Adsorbate Solution:

Stock solution of Zn(II) was prepared (1000 mgL\textsuperscript{-1}) by dissolving desired quantity of Zinc nitrate (AR grade in distilled water.

2.2.3 Adsorption Studies:

Adsorption studies were carried out by batch process. 0.5 g of adsorbent was taken in a conical flask. 50 ml solution of metal ions of desired concentration was then added and mixture was shaken in shaker. The mixture was then filtered and final concentration of metal ions was determined in the filtrate by atomic absorption spectrophotometer (Model GBC 902) using air-acetylene flame. The amount of metal ion adsorbed was calculated by subtracting final concentration from initial concentration.

2.2.4 Effect of pH:

The effect of pH on the adsorption of Zn(II) was studied as follows. 100 ml Zn(II) solution was taken in a beaker. The pH of solution was adjusted by adding dilute solution of HCl or NaOH. The concentration of Zn(II) in this solution was then determined (initial concentration). 50 ml of this solution was taken in a conical flask and treated with 0.5 g of adsorbent and after equilibrium the final concentration of Zn(II) was determined.

2.2.5 Desorption or Recovery of Zn(II):

The desorption studies were carried out by batch as well as by column process under similar conditions. 50 ml of the sample
containing 10 mg\text{L}^{-1} \text{Zn(II)} was treated with 1 g of adsorbent. The pH of the solution was adjusted to 6 and was left in contact with adsorbent for 24 h. The solution was then filtered and filtrate was analysed for Zn(II). The adsorbent was then transferred to another conical flask and treated with 50 ml of 0.05 M HCl solution. It was again filtered and the desorbed Zn(II) was determined in the filtrate. Column studies were conducted using 1 g of Teak leaves packed in glass column (0.6 cm in diameter) with a glass wool support. The adsorbent was washed with distilled water and then 50 ml solution containing 0.5 mg of Zn(II) (pH 6) was passed through the column. The adsorbed Zn(II) was then eluted with 0.05 M HCl solution with a flow rate of 1 ml min\textsuperscript{-1} throughout the elution process. Zn(II) eluted was collected in 10 ml fractions and then determined by atomic absorption spectrophotometer.

**2.2.6 Regeneration studies:**

0.5 g of adsorbent was treated with 50 ml Zn(II) solution (50 mg\text{L}^{-1}) in a conical flask and after equilibrium time it was filtered. The adsorbent was then treated with 50 ml HCl solution (0.05 M) for 24 h. It was again filtered and filtrate was analysed for Zn(II) desorbed. The adsorbent was washed several times with distilled water in order to remove excess acid. It was again treated with 50 ml Zn(II) solution and above procedure was repeated a number of times (5 times or cycle).

**2.2.7 Recovery of Zn(II) from electroplating waste water:**

The removal and recovery of Zn(II) from electroplating waste water was carried out by batch as well as by column operations. 50 ml of the
waste containing 12.9 \, \text{mgL}^{-1} \, \text{Zn(II)} \) was taken in a conical flask and its pH was adjusted to 6. It was then treated with 1 g of adsorbent. The removal and recovery of Zn(II) was carried out as described above. In another experiment, 50 ml of the waste was taken in a beaker and its pH was adjusted to 6. It was then passed through the column containing 1 g of adsorbent and the removal and recovery of Zn(II) was carried out as described above.

2.3 RESULTS AND DISCUSSION

The adsorptions of Cr(VI), Ni(II), Zn(II) and Cd(II) on Teak leaves at pH (6-7) is shown in Table 2.1. The adsorption of Cr(VI) is minimum while Zn (II) adsorbed maximum (96%). The adsorption of Cd(II) and Ni(II) is also very high. A similar behaviour was observed when phosphate treated sawdust was used (Ajmal et al., 1996) where maximum adsorption of Zn(II) and Ni(II) was observed.

2.3.1 Effect of contact time :

The dependence of adsorption of Zn(II) with time is presented in Fig. 2.1. The adsorption increases with increasing contact time. The Zn(II) uptake vs time curve at different temperatures (Fig. 2.1) shows that initially (at 15 minutes contact time ) adsorption of Zn(II) is low at 30°C and increases as the temperature is increased to 50°C. However, when contact time is increased (at 30°C) the adsorption also increases and equilibrium is attained after 2 h. When temperature is increased further (40 and 50°C) the adsorption is rapid and equilibrium is attained much earlier (30 mints). It is also important to note that adsorption of Zn(II) at
$40^\circ$ and $50^\circ$C is almost equal as the contact time is increased from 30 minutes to 1 h and after that the adsorption at $50^\circ$C is slightly increased. It can be concluded that adsorption of Zn(II) increases with the increase in temperature and equilibrium is attained earlier but uptake of Zn(II) Vs time curves at 40 and $50^\circ$C are not smooth. However at $30^\circ$C the uptake of Zn(II) is less and equilibrium time is more (2 h) but at the same time the Zn (II) uptake vs time curve is smooth and continuous leading to saturation and indicates the possibility of monolayer coverage of Zn(II) ions on adsorbent surface. A similar behaviour was observed (Prabhu et al., 1981) on the adsorption of Zn(II) by flyash.

2.3.2 Effect of Concentration:

Fig 2.2 shows that when concentration of Zn(II) is increased, the adsorption of Zn(II) also increases but at the same time % adsorption decreases. The maximum adsorption (100%) is observed at 20 mgL$^{-1}$ initial Zn(II) concentration (Fig. 2.2) and decreases to 75% when initial Zn(II) concentration is increased to 100 mgL$^{-1}$.

2.3.3 Effect of temperature on metal adsorption:

The temperature range used in this study was from 30 to $50^\circ$C. Adsorption increases with increase in temperature. Thermodynamic parameters such as free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were calculated using the following equations (Singh et al., 1988; Catena and Bright, 1989; Fraji et al., 1992):

$$K_c = \frac{C_{Ad}}{C_e}$$
where $K_c$ is equilibrium constant, $C_{Ac}$ and $C_e$ are the equilibrium concentration (mgL$^{-1}$) of the metal ion on the adsorbent and in the solution respectively.

$$\Delta G^0 = -RT \ln K_c$$

where $T$ is temperature in kelvin and $R$ is the gas constant

$$\log K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT}$$

$\Delta H^o$ and $\Delta S^o$ were obtained from the slope and intercept of Van't Hoff Plots of log $K_c$ vs 1/T (Fig. 2.3). Positive values of $\Delta H^o$ (Table 2.2) suggest the endothermic nature of adsorption. The negative values of $\Delta G^0$ indicate spontaneous nature of adsorption of Zn(II) on the adsorbent. The positive values of $\Delta S^o$ show the increased randomness at the solid/solution interface during the adsorption of metal ion on Teak leaves. The increase in adsorption capacity of Teak leaves at higher temperatures may be attributed to the enlargement of pore size or activation of the adsorbent surface (Vishwakarma et al, 1989). The values of $K_c$ are also high at all temperatures and increase when temperature is increased (Table 2.2) showing endothermic process.

2.3.4 Adsorption dynamics:

The rate constant of adsorption is determined from the following first order rate expression given by Lagergren (1989).
where \( q \) and \( q_e \) are amounts of metal adsorbed (mgg\(^{-1}\)) at time \( t \) (minute) and at equilibrium respectively and \( K_{ad} \) is the rate constant for adsorption (Lmin\(^{-1}\)). The straight line plots of \( \log (q_e-q) \) vrs \( t \) at different temperatures (Fig. 2.4) indicate the applicability of the above equation. Values of \( K_{ad} \) were calculated from the slope of the linear plots. Table 2.3 shows that adsorption rate constant increases with increase in temperature confirming the endothermic type of adsorption.

### 2.3.5 Intraparticle diffusion:

The rate constant for intraparticle diffusion (\( k' \)) is calculated by the equation of Weber and Morris (1962)

\[
\frac{C_t}{C_0} = K't^{\frac{1}{2}}
\]

Where
- \( K' \) = Rate constant for intraparticle diffusion
- \( C_t \) = concentration of metal ion at time \( t \) (mgL\(^{-1}\))
- \( C_0 \) = Initial concentration of metal ions (mgL\(^{-1}\))

The adsorption of metal ions on any porous material generally involves adsorption via intraparticle diffusion besides other processes. The occurrence of intraparticle diffusion during adsorption is confirmed by a linear plot of \( C_t/C_0 \) vrs \( t^{\frac{1}{2}} \). Fig. 2.5 shows intraparticle diffusion over a wide range of contact time but at the same time straight lines do not pass through the origin at different temperatures, indicating that
intraparticle diffusion is not the only rate limiting factor but other processes of adsorption are also involved.

2.3.6 Effect of pH :

The effect of pH on the adsorption of Zn(II) by Teak leaves is presented in Fig. 2.6. The pH of the aqueous solution is an important controlling parameter in the adsorption process (Elliot and Huang; 1981). At lower pH value the H⁺ ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions (Forstner and Wittman, 1981). Fig 2.6 Shows that appreciable amounts of Zn(II) is adsorbed in the pH range 2-6. It has been reported that at lower pH, Zn²⁺ is the predominant species present in the solution followed by ZnO⁻H and at very high pH, Zn(OH)₄⁻² is the predominant species followed by Zn(OH)₃⁻ (Sawyer et al., 1994) It can be inferred that removal of Zn(II) from aqueous solution in the pH range 2-6 involves adsorption of Zn¹² species by teak leaves and not by precipitations of Zn(II) as hydroxide.

Similar results of pH effect were reported for the adsorption of Zn(II) on flyash (Prabhu et al., 1981). However, below pH 2, the adsorption decreases very rapidly 20% at pH-1), this behaviour of adsorption and desorption by varying pH may be utilized for the recovery of Zn(II) from waste water.

2.3.7 Effect of adsorbent doses :

The adsorption densities (mgg⁻¹) and % adsorptions of Zn(II) at different doses of Teak leaves are shown in Fig. 2.7. The % adsorption
increases as the adsorbent dose is increased but adsorption density decreases from 234 mgg$^{-1}$ to 48 mgg$^{-1}$ when adsorbent dose is increased from 0.2g to 1g. It may be concluded that by increasing the adsorbent dose the removal efficiency of Teak leaves increases but adsorption density decreases. The decrease in the adsorption density may be due to the fact that some adsorption sites remain unsaturated during the adsorption process whereas the number of available adsorption sites increase by increasing the adsorbent doses and that results in the increase of removal efficiency (Sharma and Forster, 1993; Ajmal et al., 1996).

2.3.8 Desorption studies:

The adsorption of Zn(II) on Teak leaves is highly pH dependent hence its desorption is possible by controlling the pH Fig. 2.8 shows the desorption trend of Zn(II) by column operation. Zn (II) is retained in the column as long as pH of the solution is maintained at 6. The desorption starts when a solution of 0.05 M HCl is passed through the column. It is important to note that desorptions of Zn(II) is rapid and 96% Zn(II) could be eluted in 30 ml of effluent from the column. However the desorption is slow and incomplete by batch process. The desorption of Zn(II) from a solution containing 50mgL$^{-1}$ Zn(II) by batch process was 76%.

2.3.9 Regeneration Studies:

In order to make the process of adsorption and recovery of Zn (II) more economical, it is necessary to regenerate the spent adsorbent. The adsorption and desorption of Zn(II) on Teak leaves by column operation
after each regeneration cycle (by 0.05 M HCl) is shown in Table 2.4. It is interesting to note that adsorption remains maximum (99%) up to 3rd regeneration cycle and then goes down to 91.6% in the 5th cycle. The recovery or desorption of Zn(II) also remains maximum (86%) up to 3rd cycle and then decreases to 60% in the 5th cycle of regeneration. This behaviour indicates that the adsorbent can be used successfully three times after regeneration for the removal and recovery of Zn(II) from waste water.

2.3.10 Recovery of Zn(II) from electroplating waste water:

Teak leaves as an adsorbent was utilized for the removal and recovery of Zn(II) from electroplating waste water by column operation. The electroplating waste water collected from one of the electroplating industries in Aligarh (India) was analysed in our laboratory and the results are shown in Table 2.5. The removal of Zn(II) was 93.02% when 50 ml of the waste treated with 1.0 g of adsorbent. The adsorbed Zn (II) was then recovered (95.3%) with 0.05 M HCl. These results are shown in Table 2.6.

2.4 CONCLUSION

It can be concluded that Teak leaves are excellent adsorbent for Zn(II), Ni(II) and Cd(II) removal from aqueous solution. 100% removal of Zn(II) is observed at 20 mgL\(^{-1}\) initial Zn(II) concentration. The thermodynamic parameters indicate that process is endothermic and spontaneous. The adsorption of Zn(II) is pH dependent. Maximum adsorption occurs at pH 6 and decrease with the decrease in pH. This behaviour has been utilized for the recovery of Zn(II) from waste water.
96% Zn(II) can be recovered using 0.05 HCl solution by column operation. The desorption is rapid and maximum amount of Zn(II) can be desorbed in small volume of effluents (30 ml). The regeneration of the adsorbent makes the process more economical. The practical utility of the process has been demonstrated by showing the removal and recovery of Zn(II) (95.3%) from electroplating waste water contains Zn(II), Cu(II), Ni(II) and Cr(VI) ions.

Another important and significant feature of this study is that Cu(II), Ni(II) and Zn(II) show maximum adsorption while adsorption of Cr(VI) is least under similar conditions.

The electroplating waste water contains appreciable amount of Cr(VI) along with small quantities of Cu, Ni and Zn. Thus the adsorbent can be used for the purification of Cr(VI) solution by removing Cu, Ni and Zn without adjusting the pH. The electroplating waste water containing only Cr(VI) can be reused in electroplating bath or may be concentrated by some other methods. However to achieve this a detailed study on the adsorption of Cu, Ni and Cr(VI) has to be carried out on the present adsorbent.
### Table 2.1. Adsorption of different metal on Teak leaves

<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial conc. (mgL⁻¹)</th>
<th>Amount adsorbed (mgL⁻¹)</th>
<th>% adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>50</td>
<td>22</td>
<td>44</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>50</td>
<td>43.8</td>
<td>87.6</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>50</td>
<td>48</td>
<td>96</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>50</td>
<td>46.5</td>
<td>93</td>
</tr>
</tbody>
</table>

### Table 2.2. Thermodynamic parameters

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$K_c$ (X10⁻¹)</th>
<th>$\Delta G^\circ$ (KJmol⁻¹)</th>
<th>$\Delta H^\circ$ (KJmol⁻¹)</th>
<th>$\Delta S^\circ$ (KJmol⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>52.5</td>
<td>-4.156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>90</td>
<td>-5.698</td>
<td>39.251</td>
<td>0.142</td>
</tr>
<tr>
<td>50</td>
<td>24</td>
<td>-8.512</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3: Rate constant at different temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Lagergren rate const. $K_{eq}$ (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>$0.806 \times 10^{-2}$</td>
</tr>
<tr>
<td>40</td>
<td>$0.829 \times 10^{-2}$</td>
</tr>
<tr>
<td>50</td>
<td>$0.852 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Table 2.4: Effect of regeneration on the adsorption and desorption of Zn (II) by Teak leaves.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>No. of cycle</th>
<th>Amount of Zn(II) before adsorption (mgL⁻¹)</th>
<th>Amount of Zn(II) after adsorption (mgL⁻¹)</th>
<th>Adsorption %</th>
<th>Amount Zn(II) desorbed with 0.05M HCl (mgL⁻¹)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>10.00</td>
<td>0.01</td>
<td>99.9</td>
<td>9.99</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>10.01</td>
<td>0.03</td>
<td>99.7</td>
<td>9.57</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>10.04</td>
<td>0.06</td>
<td>99.4</td>
<td>8.54</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>10.14</td>
<td>0.46</td>
<td>95.4</td>
<td>6.67</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>10.74</td>
<td>0.86</td>
<td>91.6</td>
<td>5.49</td>
<td>60</td>
</tr>
</tbody>
</table>
Table 2.5: Analysis of electroplating waste water

<table>
<thead>
<tr>
<th>Metal ions/pH</th>
<th>Concentrations (mgL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (VI)</td>
<td>30</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>7.9</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>14.5</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>12.9</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>2.1</td>
</tr>
<tr>
<td>pH</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Table 2.6.  Removal and recovery of Zn(II) from electroplating waste water by batch process

Amount of adsorbent = 1 g.

<table>
<thead>
<tr>
<th>Volume of electroplating waste water (ml)</th>
<th>Amount of Zn(II) bef or adsorption (mgL⁻¹)</th>
<th>Amount of Zn(II) after adsorption (mgL⁻¹)</th>
<th>Removal %</th>
<th>Amount Zn(II) desorbed with 30 ml of 0.05M HCl (mgL⁻¹)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>12.90</td>
<td>0.90</td>
<td>93.02</td>
<td>11.44</td>
<td>95.3</td>
</tr>
</tbody>
</table>
Fig 2.1 Effect of contact time

Fig 2.2: Effect of concentration
Fig. 2.3. $\log K_c$ vs $1/T$

Fig. 2.4. Lagergren plots
Fig. 2.5: $c_t/c_0$ vs $t^{1/2}$

Fig. 2.6: Effect of pH on the adsorption of Zn(II) by Teak leaves
Fig 2.7. Effect of adsorbent doses

Fig 2.8. Recovery of Zn(II)
REFERENCES


Alan J. Rubin (Ed); *Aqueous Environmental chemsitry of metal,* p. 92 1976.


Earley, B.B. "Minor element studies with soyabean. 1. varietal reactions to concentration of Zinc in excess of the nutritional requirements". J. Agronomy, 1943, 35, 1012.


CHAPTER 3
ADSORPTION STUDIES ON CITRUS RETICULATA (FRUIT PEEL OF ORANGE): REMOVAL AND RECOVERY OF Ni(II) FROM ELECTROPLATING WASTEWATER

3.1 INTRODUCTION

Industrial, agricultural and domestic waste pollute the water bodies with heavy metals, which reach tissues through the food chain. The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years. Adsorption of trace metals onto natural particulate matter can play an important role in determining trace metal speciation in many aquatic systems (Laxen, 1983a; Jenne, 1977; Florence, 1982; Oakley et al., 1981). Among different types of pollution the industrial waste constitutes the major source of various kinds of metal pollution in natural water (Harrison, et al., 1980). The important toxic metal, i.e. Cd, Zn, Cr, Pb and Cu finds its way to the water bodies through wastewater from such industries as metal plating industries of cadmium, nickel batteries, pigment, stabilizers alloys (Low et al., 1991).

Nickel is used in plating plants and is present in their wastewater (Klein et al., 1974). About 40% of the nickel produced is used in steel factories, Ni batteries and in the production of some alloys (Friberg et al., 1980). Production of dermatitis in some workers engaged in electroplating, polishing, paints and pigments may be attributed to nickel poisoning.

The conventional methods for heavy metal removal from wastewater includes reduction, precipitation, ion exchange, reaction with
silica, electrochemical reduction, evaporation, reverse osmosis and direct precipitation. Most of these methods are high capital cost with recurring expenses which are not suitable for small-scale industries. Studies on treatment of effluents bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among the physico-chemical treatment processes.

Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost materials. Polymerized onion skin with formaldehyde (Kumar et al., 1981), waste wool (Friedman et al., 1973; Friedman et al., 1972; Nasri et al., 1973), peanut skin (Randall et al., 1975; Randall et al., 1978), modified barks (Randall et al., 1974; Randall et al., 1976), barks (Kumar et al., 1980), barley straw (Larsen et al., 1981) have been studied. Removal of nickel by adsorption using solid residue form olive mill products (Gharaibeh et al., 1998), mangifera indica seed shell (Ajmal et al., 1998), humic acid type purifying agents (Guangju, et al., 1986), coal based adsorbents (Singh et al., 1992), burned clay and root (Donali et al., 1992), furnace gas cleaning sludge (Jallan et al., 1992), hydrous oxides of iron(II) (Kanungo, 1994) have been reported.

It is possible to process the solid residue of orange fruit peel and convert it to an adsorbent that has a large surface area and thus great potential to adsorb harmful contaminants, such as heavy metals from aqueous solutions and industrial waste at relatively low cost compared with other available adsorbents.
3.2 MATERIAL AND METHODS

3.2.1 Adsorbent:

Sieved fruit peel of Citrus reticulata (orange fruit) was used for the removal of Ni(II) from aqueous solution. The fruit peels were dried, crushed and washed thoroughly with double distilled water to clear the adhering dirt and finally dried in an air oven at 100-105°C for 24 h. After drying the adsorbent was sieved through 150-mesh size and used as such.

3.2.2 Adsorbate Solution:

Stock solution of Ni(II) was prepared (1000 mgL\(^{-1}\)) by dissolving desired quantity of Nickel nitrate (AR Grade) in distilled water. Solution of other metal ions were prepared (1000 mgL\(^{-1}\)) by dissolving their chlorides or nitrates.

3.2.3 Adsorption Studies:

Adsorption studies were carried out by batch process. A 0.5 g of adsorbent was placed in a conical flask in which 50ml solution of metal ion of desired concentration was added and mixture was shaken in shaker. The mixture was then filtered and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (model GBC 902). The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration.

3.2.4 Effect of pH:

The effect of pH on the adsorption of Ni (II) was studied as described in chapter 2.
3.2.5 Desorption of Ni(II):

The desorption studies were carried out by batch as well as by column process under similar conditions. 50 ml of the sample containing 10 mg mL\(^{-1}\) Ni(II) was treated with 1 g of adsorbent. The pH of the solution was adjusted to 6 and was left in contact with adsorbent for 24 h. The solution was then filtered and filtrate was analyzed for Ni(II). The adsorbent was then transferred to another conical flask and treated with 50 ml of 0.05 M HCl solution. It was again filtered and desorbed Ni(II) was determined in the filtrate. The column studies were conducted using 1 g of orange fruit peel in a glass column (0.6 cm in diameter) with a glass wool support. The adsorbent was washed with distilled water and 50 ml solution containing 0.5 mg of Ni(II) (pH 6) was passed through the column. The Ni(II) adsorbed was then eluted with 0.05 M HCl solution with a flow rate of 1 ml min\(^{-1}\). Ni(II) eluted was collected in 10 ml fractions and then determined by atomic absorption spectrophotometer.

3.2.6 Regeneration Studies:

A 0.5 g of adsorbent was treated with 50 ml Ni(II) solution (50 mg mL\(^{-1}\)) in a conical flask and after equilibrium time it was filtered. The adsorbent was then treated with 50 ml HCl solution (0.05 M) for 24 h. It was filtered and filtrate was analysed for Ni(II) desorbed. The adsorbent was washed several times with distilled water in order to remove excess acid. It was again treated with 50 ml Ni(II) solution and the above procedure was repeated a number of times (5 times or cycle).
3.2.7 Recovery of Ni(II) from electroplating wastewater:

The removal and recovery of Ni(II) from electroplating wastewater was carried out by batch as well as by column operations. 50 ml of the waste containing 10 mg l⁻¹ Ni(II) was taken in a conical flask and its pH was adjusted to 6 and then treated with 1 g of adsorbent. The removal and recovery of Ni(II) was carried out as described above. In another experiment 50 ml of the waste was taken in a beaker and its pH was adjusted to 6. It was then passed through the column containing 1 g of adsorbent and the removal and recovery of Ni(II) was carried out as described above.

3.3 RESULT & DISCUSSION

The % adsorption behaviour of different metal ions on orange fruit peel shows that the adsorption of Ni(II) is maximum (97.5%) while Cr(VI) adsorbed least (30%) Fig. 3.2. The % adsorption follows the order

\[ \text{Ni(II)} > \text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Cr(VI)}. \]

3.3.1 Effect of Contact Time:

The adsorption increases with increasing contact time. The Ni(II) uptake vs. time curve at different temperatures (Fig. 3.1) shows that initially (at 15 minutes contact time) the adsorption of Ni(II) is low at 30°C and increases as the temperature is increased to 50°C. However, when contact time is increased at 30°C, the adsorption also increases and equilibrium is attained after 2h. Maximum uptake of Ni(II) occurs at 50°C but equilibrium time remains the same (2h). The metal uptake vs. time curves at different temperature are single, smooth and continuous leading
to saturation, suggesting possible monolayer coverage of metal ions on the surface of the adsorbent.

3.3.2 Effect of Concentration:

The effect of concentration on the adsorption behaviour of metal ions is shown in Fig. 3.2. It can be concluded that maximum adsorption of Ni(II), Cu(II), Zn(II) and Pb(II) occurs at 40 mgL$^{-1}$ initial concentration whereas the adsorption of Cr(VI) remains minimum over a wide range of concentration (20-100 mgL$^{-1}$). However at lower concentration (20 mgL$^{-1}$) the adsorption follows the order:

Ni(II) > Pb(II) > Zn(II) > Cu(II) > Cr(VI)

and at higher concentration (100 mgL$^{-1}$) the adsorption behaviour follows the order

Ni(II) > Cu(II) > Pb(II) > Zn(II) > Cr(VI)

showing that % adsorption of Ni(II) remains maximum over a wide range of initial concentration while adsorption of Cr(VI) is least under similar conditions.

3.3.3 Effect of temperature on metal adsorption:

The temperature range used in this study was from 30 to 50°C. Adsorption increases with increase in temperature. Thermodynamic parameters such as standard free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) were calculated using the following equations (Singh et al., 1988; Catena et al., 1989; Fraji, et al. 1992).
where \( K_c \) is the equilibrium constant

\[
K_c = \frac{C_{Ac}}{C_e}
\]

\( C_{Ac} \) and \( C_e \) are the equilibrium concentration (mgL\(^{-1}\)) of the metal ion on the adsorbent and in the solution respectively. \( \Delta G^0 \) was calculated from the relation

\[
\Delta G^0 = -RT \ln K_c
\]

where \( T \) is temperature in Kelvin and \( R \) is gas constant. \( \Delta H^0 \) was calculated from the following equation

\[
\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}
\]

\( \Delta H^0 \) and \( \Delta S^0 \) were obtained from the slope and intercept of Van't Hoff plots of \( \log K_c \) vs. \( 1/T \) (Fig. 3.3). Positive values of \( \Delta H^0 \) (Table 3.1) suggest the endothermic nature of adsorption. The negative values of \( \Delta G^0 \) indicate spontaneous nature of adsorption of Ni(II) on the adsorbent. The positive value of \( \Delta S^0 \) show the increased randomness at the solid/solution interface during the adsorption of metal ion on fruit peel of orange. The increase in adsorption capacity of fruit peel of orange at higher temperature may be attributed to the enlargement of pore size or activation of the adsorbent surface (Viswakarma et al., 1989). The values of \( K_c \) are also high at all temperature and increase with rise in temperature (Table 3.1) showing endothermic process.
3.3.4 Adsorption Isotherms:

The adsorption data has been analysed in the light of Langmuir and Freundlich adsorption models. The Langmuir equation may be described as

\[
\frac{1}{x/m} = \frac{1}{\theta_0 b} \cdot \frac{1}{C_e} + \frac{1}{\theta_0}
\]

where \(x/m\) is metal uptake per unit weight of adsorbent, \(C_e\) is the equilibrium concentration of metal (mgL\(^{-1}\)), \(\theta_0\) and \(b\) are Langmuir constants relating to adsorption capacity and adsorption energy respectively. The Langmuir isotherm is valid for monolayer adsorption onto the surface of the adsorbent containing a finite number of identical sites. The plot of \(1/x/m\) against \(1/C_e\) gives straight line (Fig. 3.4) at each temperature showing the applicability of Langmuir isotherm. The adsorption capacity (\(\theta_0\)) for the uptake of Ni(II) increases from 80 mg g\(^{-1}\) to 158 mg g\(^{-1}\) by increasing temperature from 30 to 50°C showing the process to be endothermic. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (\(R_L\)) which is defined by the following relation:

\[
R_L = \frac{1}{1 + b \cdot C_0}
\]

where \(C_0\) is the initial metal ion concentration (mgL\(^{-1}\)) and \(b\) is the Langmuir constant. The \(R_L\) values at 30, 40 and 50°C are found to be
0.057, 0.0542 and 0.0848 respectively showing favourable adsorption of Ni(II) (Namasivayam et al., 1995; Poots et al., 1978).

The Freundlich adsorption isotherm was also applied for the adsorption of Ni(II)

\[
\ln \frac{x}{m} = \ln K_f + \frac{1}{n} \ln C_e
\]

where \( C_e \) is the equilibrium concentration (mgL\(^{-1}\)), \( X/m \) is the amount adsorbed per unit weight of adsorbent (mgL\(^{-1}\)). \( K_f \) and \( n \) are Freundlich constants. The linear plot of \( \ln(x/m) \) vs. \( \ln C_e \) at each temperature indicates that adsorption of Ni(II) also follows Freundlich isotherm (Fig. 3.5).

The values of Langmuir and Freundlich constants at different temperatures are shown in Table 3.2. The increase in \( K_f \) values with rise in temperature also confirms that the process is endothermic (Table 3.2).

### 3.3.5 Adsorption Dynamics:

The rate constant of adsorption is determined from the following first order rate expression given by equation (Lagergren et al., 1898).

\[
\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} \times t
\]

Where \( q \) and \( q_e \) are amounts of metal adsorbed (mg g\(^{-1}\)) at time, \( t \) (min.) and at equilibrium respectively and \( K_{ad} \) is the rate constant for adsorption (Lmin\(^{-1}\)). The straight line plots of \( \log (q_e - q) \) vs. \( t \) at different temperatures (Fig. 3.6) indicate the applicability of the above equation. Values of \( K_{ad} \) were calculated from the slope of the linear plots. Table 3.3 shows the adsorption rate constant is not affected with increase in temperature.
3.3.6 Intraparticle Diffusion:

The rate constant for Intraparticle diffusion ($K'$) is calculated by the equation (Weber et al., 1962).

$$q = K' t^{1/2}$$

Where $q$ is the amount adsorbed (mg g$^{-1}$) at time, $t$ (min). Plots of $q$ vs. $t^{1/2}$ are shown in Fig. 3.7 for different temperatures. $K'$ values were obtained from the slope of the linear portion of the curves for each temperature (Table 3.3). $K'$ values increase when temperature is increased from 30° to 50°C.

3.3.7 Effect of pH:

The effect of pH on the adsorption of Ni(II) by fruit peel orange is presented in (Fig. 3.8). The pH of the aqueous solution is important controlling parameters in the adsorption process (Elliot et al., 1981). At lower pH value, the H$^+$ ions compete with metal cation for the exchange sites in the system thereby partially releasing the later. The heavy metal cations are completely released under circumstances of extreme acidic conditions (Forstner et al., 1981; Sharma et al., 1993; Ajmal et al., 1996, 1998). The % adsorption is minimum (40%) at pH 2 and increase as the pH is increased. The maximum adsorption occurs at pH 6 (97.5%) but adsorption decreases when pH is increased further. The minimum adsorption at low pH (pH 2) may be due to the fact that high concentration and high mobility of H$^+$ ions, the hydrogen ions are preferentially adsorbed compared to Ni(II) ions.
3.3.8 Desorption Studies:

The adsorption of Ni(II) on fruit peel of orange is highly pH dependent hence its desorption is possible by controlling the pH. Fig. 3.9 shows the desorption trend of Ni(II) by column operation. Ni(II) is retained in the column as long as pH of the solution is maintained at 6. The desorption starts when a solution of 0.05 M HCl is passed through the column. It is important to note that desorption of Ni(II) is rapid and 95.83% Ni(II) could be eluted in 30 ml of effluent from the column. However, the desorption is slow and incomplete by batch process. The desorption of Ni(II) from a solution containing 50 mgL⁻¹ Ni(II) by batch process was 76% (Table 3.4).

3.3.9 Regeneration Studies:

In order to make the process of adsorption and recovery of Ni(II) more economical, it is necessary to regenerate the spent adsorbent. The adsorption and desorption of Ni(II) on fruit peel of orange by column operation after each regeneration cycle (by 0.05 M HCl) is shown in Table 3.4. It is interesting to note that adsorption remains maximum (98%) upto the 3rd regeneration cycle and then goes down to 95% in the 4th cycle. The recovery or desorption of Ni(II) also remains maximum (90%) upto the 3rd cycle and decreases to 70% in the 4th cycle of regeneration. This behaviour indicates that the adsorbent can be used successfully 4 times after regeneration for the removal and recovery of Ni(II) from wastewater.

3.3.10 Recovery of Ni(II) from Electroplating Wastewater:

Fruit peel of orange as an adsorbent was utilized for the removal and recovery of Ni(II) from electroplating wastewater by column operation.
The electroplating wastewater collected from one of the electroplating industries in Aligarh (India) was analyzed in our laboratory and the results are shown in Table 3.5. The adsorbed Ni(II) was recovered (93.33%) with 0.05M HCl. These results are shown in Table 3.6.

3.4 CONCLUSION

The fruit peel of orange (Citrus reticulata) is a low cost adsorbent which is abundantly available in India as waste material. It can be used as an effective adsorbent for the removal and recovery of Ni(II) from waste water. The adsorption of Ni(II) is pH dependent and maximum removal occurs at pH 6. The adsorption follows first order Kinetics. The process is endothermic and follows Langmuir and Freundlich isotherm. The adsorbed Ni(II) can be recovered using 0.05 M HCl solution. However, the recovery of Ni(II) by column operation is higher (95.8%) as compared to batch process (76%). The spent adsorbent can be regenerated and reused making the adsorption process more economical.
Table 3.1 Thermodynamic Parameters for adsorption of Ni(II)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$K_c$</th>
<th>$\Delta G^0$ (KJmol$^{-1}$)</th>
<th>$\Delta H^0$ (KJmol$^{-1}$)</th>
<th>$\Delta S^0$ (K JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6.14</td>
<td>-4.7226</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>11.5</td>
<td>-6.5586</td>
<td>53.89</td>
<td>0.1923</td>
</tr>
<tr>
<td>50</td>
<td>24</td>
<td>-8.7984</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp. 0°C</td>
<td>Langmuir Constants</td>
<td>Freundlich Constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
<td>---------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>$b$</td>
<td>$\theta^0$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>30</td>
<td>0.9564</td>
<td>0.3298</td>
<td>80</td>
<td>0.9861</td>
</tr>
<tr>
<td>40</td>
<td>0.9886</td>
<td>0.3489</td>
<td>89.2857</td>
<td>0.9652</td>
</tr>
<tr>
<td>50</td>
<td>0.9727</td>
<td>0.2157</td>
<td>158.7301</td>
<td>0.983</td>
</tr>
</tbody>
</table>
Table 3.3. Rate constant at different temperature for adsorption of Ni(II)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Lagergren rate constant $K_{ad}$ (Lmin⁻¹)</th>
<th>Intraparticle rate constant $K'$ (mgg⁻¹min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.750x10⁻²</td>
<td>1.1238</td>
</tr>
<tr>
<td>40</td>
<td>2.049x10⁻²</td>
<td>2.2432</td>
</tr>
<tr>
<td>50</td>
<td>1.934x10⁻²</td>
<td>3.8063</td>
</tr>
<tr>
<td>S.No.</td>
<td>No. of cycle</td>
<td>Amt. of Ni(II) Before Adsorption (mgL⁻¹)</td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>10.0</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>10.0</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>11.18</td>
</tr>
</tbody>
</table>
Table 3.5 Analysis of electroplating wastewater

<table>
<thead>
<tr>
<th>Metal ions/pH</th>
<th>Concentration (mgL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>30.0</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>7.9</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>14.5</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>12.9</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>2.1</td>
</tr>
<tr>
<td>pH</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Table 3.6  Removal and recovery of Ni(II) from electroplating wastewater (batch process)
Amount of Adsorbent = 1 g

<table>
<thead>
<tr>
<th>Volume of Electroplating wastewater (ml)</th>
<th>Amt. of Ni(II) before adsorption (mgL(^{-1}))</th>
<th>Amt. of Ni(II) after adsorption (mgL(^{-1}))</th>
<th>% Removal</th>
<th>Amt. of Ni(II) desorbed with 0.05 M HCl (mgL(^{-1}))</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>14.5</td>
<td>1.5</td>
<td>89</td>
<td>12.62</td>
<td>93.3</td>
</tr>
</tbody>
</table>
Fig. 3.1 Effect of contact time

Fig. 3.2 Effect of concentration
Fig. 3.3 $\ln K_c$ vs $1/T$

Fig. 3.4 Langmuir Isotherm
Adsorption of Ni(II)

Fig. 3.5 Freundlich isotherm

Fig. 3.6 Lagergren plot
Fig. 3.7 Intraparticle diffusion

Fig. 3.8 Effect of pH
Fig. 3.9 Desorption of Ni(II)
REFERENCE


CHAPTER 4
CHAPTER 4

REMOVAL AND RECOVERY OF Cd(II) FROM AQUEOUS SOLUTION BY (TECTONA GRANDIS) TEAK LEAVES

4.1 INTRODUCTION

Currently more than 50% of the nation's population relies on ground water sources that are in potential danger of contamination (Venkata Ramani et al., 1984). There has been increasing concern over dangerous levels of heavy metals contaminating the aquatic environment and sources of potable water because of their known accumulation in the food chain and their persistence in nature when they are discharged in small quantities by numerous industrial activities. Cadmium is very toxic element that causes high blood pressure, kidney damage and destruction of blood cells in human even in small doses (Manahan, 1991).

A small part of Cd annual production of around 18,000 tons per year (Porteous, 1992) ends up in the environment through industrial discharge. Toxic heavy metal ions are also frequently found in landfill leachates, in which the most prevalent ones are Cadmium, Copper, Lead and Mercury, (Barker et al. 1986). Various technologies are employed for removal of toxic ions from water, which include chemical precipitation, reverse osmosis, ions floatation, evaporation, ion exchange and adsorption (Rawat and Singh, 1992). Sorption technology based on ion exchange processes through physical and chemical sorption has been found increasing applications in various fields during the past few year. The use of sorption process for the removal of heavy metals from wastewater is especially promising. The preparation of low cost adsorbent
for water purification and waste water treatment has recently been received (Pollard et al., 1992) attention for example alginic acid has shown to be effective for removal of many cationic metal from solution including Cu\[^2+\], Zn\[^2+\], Cd\[^2+\], and Ni\[^2+\] (Jellinck and Sangal, 1972). Biosorption of Cadmium(II) by algal biomass (Chu et. al., 1997) and dead biomass from aqueous solution has been studied (Matis et al., 1997). Some small scale cultivation tests (50 L) with Cd-resistant cell of chlorella vulgaris have been able to remove ~ 40% Cd \text{L}^{-1} solution within 7 days (Sandau et. al., 1996). Adsorption of Cd(II) and Pb (II) on agricultural byproducts (Jahagirdar et al., 1997) and the use of fibrous sorbent showed a fairly high effectiveness in removing Cr, Cd, Zn, and Cu ions from electroplating wastewater, (Burinski, 1996). Cadmium biosorptions by pseudomonas putida entrapped in gel beads of sugar beat pectin has also been carried out (Harel et. al., 1997). The behaviour of some adsorbents like silica gel, pyrolusite, Fe(III) hydroxide and saw dust for the removal and recovery of Pb\[^2+\], Cr\[^3+\], Ni\[^2+\], Cu\[^2+\] and Mg\[^2+\] from river and industrial waste water have been studied in our laboratory (Ajmal et. al., 1989, 1993, 1995, 1996). The study of the feasibility of Cd(II) removal by teak leaves an unconventional natural adsorbent is presented in this chapter.

Much attention has been paid to optimise the effective abatement condition in a cost-effective manner to remove the cadmium from wastewater for their safe disposal. Teak leaves, one of the cheapest and most abundantly available adsorbent has been tried for the uptake of cadmium(II) from aqueous solutions. The effect of retention time, pH,
temperature, concentration, dose, particle size on the removal of Cadmium(II) by Teak leaves have been investigated. The adsorption isotherm and the probable mechanism have been explained. The appropriate thermodynamic parameter viz. InK, ΔG, ΔS and ΔH have also been calculated and described.

4.2 MATERIAL AND METHODS

4.2.1 Adsorbent:

The grinded leaves of Tectona grandis (Teak leaves) were used as an adsorbent for the removal of Cadmium(II) from aqueous solutions. The grinded leaves were washed to clean the adhering dirt, rinsed thoroughly with doubled distilled water and finally heated in an air oven at 40°C for 24 h. After drying, the adsorbent was sieved through 100-150 mesh size and used as such.

4.2.2 Adsorbate Solution:

The stock solution of Cd(II) was prepared (1000 mgL⁻¹) by dissolving Cd(NO₃)₂ in double distilled water. All other reagents were of analytical grade.

4.2.3 Batch Adsorption Studies:

Batch adsorption experiments were carried out by shaking 0.5 g of the grinded Teak leaves with 50 ml aqueous solution of Cadmium(II) of desired concentration at various pH (1-12) and at temperatures (20°C-40°C) in different stoppered bottles for different times using a temperature controlled shaker. At the end of the predetermined time interval the adsorbent was removed by filtration and the equilibrium
concentration was estimated with atomic absorption spectrophotometer (model GBC 902) using oxyacetylene flame. Blanks were also prepared to find out the adsorption on the internal surface of bottles if any.

4.2.4 Effect of pH:

The effect of pH on the adsorption of Cd(II) was studied as follows: 100 ml Cd(II) solution was taken in a beaker. The pH of solution was adjusted by adding dilute solution of HCl or NaOH. The concentration of Cd(II) in this solution was then determined (initial concentration). 50 ml of this solution was taken in a conical flask and treated with 0.5 g of adsorbent and after equilibrium the final concentration of Cd(II) was determined.

4.2.5 Adsorption Model:

To quantify the adsorption capacity of Teak leaves for the removal of Cd(II) from water, the Langmuir and Freundlich models were used.

4.2.5.1 Langmuir Model:

Largmuir (1918) proposed the following model.

\[
\frac{1}{x/m} = \frac{1}{\theta^0 \cdot b} + \frac{1}{C_e \cdot \theta^0}
\]

where, \(C_e\) is the equilibrium concentration and \(x/m\) is the amount adsorbed per specified amount of adsorbent (mg g\(^{-1}\)). \(\theta^0\) and \(b\) are constants related to adsorption capacity and energy of adsorption respectively.

4.2.5.2 Freundlich Model:

According to this model (Freundlich 1907)
\[
\log \frac{x}{m} = \log K_t + \frac{1}{n} \log C_e
\]

where all the terms have the usual significance and \( n \) is an empirical constant. Thus a plot of \( \log x/m \) vs \( \log C_e \) should be a straight line with a slope \( 1/n \) and intercept \( \log K_t \). This model deals with the multilayer adsorption of a substance on the adsorbent. The points in Fig. 4.5 and 4.6 indicate the observed data and the line corresponds to the fitted data. A computer simulation technique has been applied to fit the freundlich and Langmuir equations for the adsorption data. The coefficient of least square fitting to a straight-line \( (R^2) \) were computed for these two models.

The rate constant of adsorption and pore diffusion were determined at 20\(^\circ\)C by using equation of Lagergren (1898) and Weber and Morris (1962).

4.2.6. Desorption of Cd(II):

The desorption studies were carried out by batch as well as by column process under similar conditions. 50 ml of the sample containing 10 mg/L \( \text{Cd}^{\text{II}} \) was treated with 1 gm of adsorbent. The pH of the solution was adjusted to 6. It was left in contact with adsorbent for 24 h. The solution was then filtered and the filtrate was analysed for \( \text{Cd}^{\text{II}} \). The adsorbent was then transferred to another conical flask and treated with 50 ml of 0.05 M HCl solution. It was again filtered and desorbed \( \text{Cd}^{\text{II}} \) determined in the filtrate. Column studies were conducted using 1 g of Teak leaves packed in glass column (0.6 cm id) with a glass wool support. The adsorbent was washed with distilled water and then 50 ml solution containing 0.5 mg of \( \text{Cd}^{\text{II}} \) (pH 7) was passed through the column. The \( \text{Cd}^{\text{II}} \) adsorbed was then eluted with 0.05 M HCl solution with a flow rate
of 1 ml min⁻¹ throughout the elution process. Cd(II) eluted was collected in 10 ml fractions and then determined by atomic adsorption.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of Concentration:

Fig. 4.1 shows that when concentration of Cd(II) is increased the adsorption of Cd(II) also increases but at the same time % adsorption decreases. The maximum adsorption (93%) is observed at 20 mgL⁻¹ initial Cd(II) concentration (Fig. 4.1) and decreases to only 81% when initial Cd(II) concentration is increased to 100 mgL⁻¹.

4.3.2 Effect of Contact Time:

The dependence of adsorption of Cadmium(II) with time is presented in Fig. 4.2. The adsorption increases with increasing contact time and the equilibrium is attained after shaking for 2 h. Therefore in each experiments the shaking time was set to 2 h. The Cd(II) uptake vs time curve is smooth and continuous leading to saturation and indicates the possibility of mono layer coverage of Cd(II) ions on adsorbent surface. A similar behaviour was observed by Namasivayam, et al., (1995) on adsorption of Cd(II) by Fe(III) hydroxides.

4.3.3 Effect of temperature on metal adsorption:

The temperature range used in this study was from 30 to 50°C. Adsorption increases with increase in temperature. Thermodynamic parameters such as free energy change (ΔG⁰), enthalpy change (ΔH⁰) and entropy change (ΔS⁰) were calculated using the following equations (Singh et al; 1988, Catena and Bright.
where $K_c$ is equilibrium constant. $C_{AC}$ and $C_e$ are the equilibrium concentration (mgL$^{-1}$) of the metal ion on the adsorbent and in the solution respectively.

$$\Delta G^0 = -RT \ln K_c$$

where $T$ is temperature in kelvin and $R$ is the gas constant.

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$

$\Delta H^0$ and $\Delta S^0$ were obtained from the slope and intercept of Van't Hoff Plots of $\log K_c$ vs $1/T$ (Fig. 4.3). Positive values of $\Delta H^0$ (Table 4.1) suggest the endothermic nature of adsorption. The negative values of $\Delta G^0$ indicate spontaneous nature of adsorption of Cd(II) on the adsorbent. The positive values of $\Delta S^0$ show the increased randomness at the solid/solution interface during the adsorption of metal ion on Teak leaves. The increase in adsorption capacity of Teak leaves at higher temperatures may be attributed to the enlargement of pore size or activation of the adsorbent surface (Vishwakarma et al.; 1989). The values of $K_c$ are also high at all temperatures and increase when temperature is increased (Table 4.1) showing endothermic process.

### 4.3.4 Effect of pH

Fig 4.4 shows that adsorption of Cd(II) on Teak leave increases when pH of the system is increased from 3 to 8 but after that adsorption is
slightly increased. It has been reported by various authors that the adsorption of metal ions depend upon the nature of adsorption and distribution of metal species in the system which in turn depend upon the pH of the system. The primary metal ion species present in the pH range 2-8 are Cd$^{2+}$ and CdOH$^+$ (Elliot et al, 1982). The negligible adsorption at pH 2 occurs because protons complete with the metal ions for the sorption site on the adsorbent. Namasivayam, 1995 has reported precipitation curve at different pH values in the absence of adsorbent and it has been found that precipitation start at pH 8.2 but only 6-10% Cd(II) is removed by precipitation in the pH range 8-8.5.

It can be concluded that maximum adsorption of Cd(II) in the form of Cd$^{2+}$ and or CdOH$^+$ occurs in the pH range 3-8. When pH is increased further (8-8.5) adsorption process still dominates over precipitation since removal of Cd(II) by adsorption is much greater than precipitation. The negligible adsorption at pH(2) is important since this property cab be utilized for the recovery (desorption) of Cd(II) from Waste water.

### 4.3.5 Adsorption Isotherms:

The adsorption data are described by Langmuir and Freundlich isotherm (Fig 4.5 and 4.6). The Langmuir isotherm in valid for monolayer adsorption onto the surface containing a finite number of identical sites. The plot of $1/x/m$ vs $1/C_e$ is linear showing the applicability of Langmuir isotherms. The values of regression coefficients, $R^2$ at 20, 30 and 40°C are 0.9995, 0.9992 and 0.9987 respectively.

The adsorption of Cd(II) also follows Freundlich isotherm (Fig 4.6). The values of Freundlich constants ($K_f$) is also very high and...
increases with the increase in temperature indicating that Cd(II) ions are strongly adsorbed and adsorption increases with the increase in temperature.

4.3.6 Adsorption dynamics:

The rate constant of adsorption and pore diffusion were determined at 20°C using equation of Lagergren (1898) and Morris (1962) respectively.

\[
\log (q_e - q) = \log q_e - \frac{K_{ad}}{2.303} \cdot t
\]

Where:
- \( q_e \) = amount of Cd(II) adsorbed at equilibrium (mgg\(^{-1}\))
- \( q \) = amount of Cd(II) adsorbed at time \( t \) (mgg\(^{-1}\))
- \( K_{ad} \) = rate constant of adsorption (Lmin\(^{-1}\))
- \( t \) = time (min)

\[
\frac{C_t}{C_0} = K' \cdot t^{\frac{1}{2}}
\]

\( C_t \) = Concentration of Cd(II) at time \( t \) (mgL\(^{-1}\))

\( C_0 \) = Initial concentration of Cd(II) (mgL\(^{-1}\)).

\( K' \) = Rate constant of pore diffusion

A linear plot of \( \log (q_e - q) \) vs \( t \) (Fig. 4.7) suggests the applicability of Lagergren equation. The rate constant of adsorption is summarized in Table 4.3.

The plot of \( \frac{C_t}{C_0} \) vs \( t^{1/2} \) (Fig. 4.8) though linear over a wide range of contact provide but does not pass through the origin, indicating that the pore diffusion is not the only rate controlling step (Poots et. al., 1978). \( K' \) values at different temperature is given in Table 4.3.
4.3.7 Effect of Adsorbent dose :

The effect of adsorbent dose on the adsorption properties of Teak leaves has been studied at pH 6 at a fixed initial Cd (II) concentration (5 mgL$^{-1}$) at different temperatures. Fig 4.9 shows that % adsorption increases with temperature when adsorbent dose is increased.

The effect of temperature is more pronounced at lower value of adsorbent doses and becomes insignificant when adsorbent does is increased beyond 0.6 gms.

4.3.8 Effect of particle size :

The studies were also carried out by using grinded Teak leaves of different particle sizes. It is evident from the results summarized in Table 4.4 that the adsorption of Cd(II) decreases with increase in particle size and peak value was observed by the finest particle (150 μ), probably because of the larger surface area.

4.3.9 Desorption Studies :

The adsorption of Cd(II) is pH dependent hence its desorption is possible by controlling pH. Fig. 4.10 shows the desorption profile by column operation. Cd(II) is retained in Column at pH 6 but desorption starts when a solution of 0.05 M HCl is passed through the column. It is interesting to note that desorption of Cd(II) is rapid and maximum Cd(II) is recovered within first fraction (84%), while complete recovery is observed in four fractions (40 ml). However, in batch process, recovery of Cd(II) is slow and incomplete (86%) when desorption was carried out with 50 ml of 0.05 M HCl solution.
4.4 CONCLUSION

i) The adsorption of Cd(II) is spontaneous and exothermic hence removal is favoured at lower temperature.

ii) The adsorption is pH dependent hence desorption of Cd(II) is possible by controlling pH of the solution.

iii) The desorption is slow and incomplete (86%) when 0.05 M HCl is used as desorbing agent in a batch reactor system. However, recovery of Cd(II) is maximum (99.3%) when 0.05 M HCl is used as desorbing agent in column process.

iv) Maximum removal of Cd(II) occurs at pH 6 hence preadjustment of pH in industrial waste water is not required.
<table>
<thead>
<tr>
<th>Temp °C</th>
<th>$K_C$</th>
<th>$\Delta G^0$ (KJmol$^{-1}$)</th>
<th>$\Delta S^0$ (KJK$^{-1}$mol$^{-1}$)</th>
<th>$\Delta H^0$ (K Jmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>32.3</td>
<td>-9.187</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>49.0</td>
<td>-10.612</td>
<td>0.138</td>
<td>35.184</td>
</tr>
<tr>
<td>40</td>
<td>91.0</td>
<td>-12.676</td>
<td></td>
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</table>

Table 4.2 Freundlich constants at different temperatures

<table>
<thead>
<tr>
<th>Temperature 0°C</th>
<th>Freundlich Constants</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$K_f$</td>
</tr>
<tr>
<td>20</td>
<td>0.9776</td>
<td>124.45</td>
</tr>
<tr>
<td>30</td>
<td>0.9593</td>
<td>223.97</td>
</tr>
<tr>
<td>40</td>
<td>0.9936</td>
<td>289.86</td>
</tr>
</tbody>
</table>
Table 4.3. Rate constant at different temperature for adsorption of Cd(II)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Lagergren rate constant ( K_{aq} ) (Lmin(^{-1}))</th>
<th>Intraparticle rate constant ( K' ) (mgg(^{-1})min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.84</td>
<td>0.0325</td>
</tr>
<tr>
<td>40</td>
<td>1.84</td>
<td>0.0284</td>
</tr>
<tr>
<td>50</td>
<td>1.84</td>
<td>0.0284</td>
</tr>
</tbody>
</table>

Table 4.4 Effect of particle size on the adsorption process.

<table>
<thead>
<tr>
<th>Particle size ((\mu))</th>
<th>% Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>99.8</td>
</tr>
<tr>
<td>200</td>
<td>97.4</td>
</tr>
<tr>
<td>250</td>
<td>95.0</td>
</tr>
<tr>
<td>300</td>
<td>83.0</td>
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<tr>
<td>350</td>
<td>62.2</td>
</tr>
<tr>
<td>400</td>
<td>46.8</td>
</tr>
</tbody>
</table>
Fig. 4.1 Effect of concentration on the adsorption of Cd(II) by Teak leaves.

Fig. 4.2 Effect of contact time.
Fig 4.3 Plot of log \( K_c \) vs 1/T

Fig 4.4 Effect of pH on the Cd (II) sorption capacity of Teak leaves
Fig. 4.5 Langmuir Isotherms

Fig. 4.6 Freundlich Isotherms
Fig 4.7 Lagergren Plot

Fig 4.8 Weber plot for intra particle diffusion
Fig 4.9 Effect of adsorbent doses

Fig 4.10 Recovery of Cd (II)
REFERENCES


Burinskii S. V.; Khim Volokna 1996 (6), 16-19 Russ Khimi Cheskie Volokna


Freundlich H.; *Phys. Chem.* 1907, 57, 384.


CHAPTER 5
CHAPTER 5

ADSORPTION BEHAVIOUR OF SOME AROMATIC AMINES ON PYROLUSITE AND ACTIVATED CARBON AND RECOVERY OF \(\beta\)-NAPHTYLAMINE FROM WATER SAMPLE

5.1 INTRODUCTION

Detection and determination of organic compounds in surface waters have received considerable attention in recent years. The development of analytical methods has led to the discovery of certain compounds in water which despite their low concentration cause damaging effect. Biological Oxygen Demand (BOD) and Chemical Oxygen demand (COD) were the methods used to quantify organic matter in water. However, these methods failed to quantify the organic compounds when present in traces. Since BOD and COD methods are based upon the effect of organic compounds on the balance of oxygen in water.

The identification and quantification of toxic organic compounds at very low concentration in water has led to the development of a new generation of analytical methods like high performance liquid chromatography and gas liquid chromatography. However, the advantage of HPLC over gas chromatography is its application in direct analysis of high molecular weight, thermally unstable and non-volatile organic compounds.

High performance liquid chromatography has been used for the separation of polynuclear aromatic hydrocarbons in water (Hunt et al., 1977; Organ et al. 1979) and drinking water (Thruston, 1978) and in
natural waters. (Jolly et al., 1975; Derenbach et al., 1978). A large number of organic compounds have been identified in Gallego river, Spain using a concentration technique with various solid supports (activated carbon: XAD-2 resin) followed by solvent extraction (Infante et al., 1993). Hydroxyaluminium inter-layered clay has been used for the separation of chlorophenols (Albans et al., 1997). Adsorption of various organic compounds on granular activated carbon has been reported (Hazousli et al., 1996; Swamy et al., 1997). Various low cost adsorbents like activated bauxite, fuller's earth and synthetic clay have been utilized for the removal of textile dyes and pesticides from wastewater and compared with activated carbon (Lambert et al., 1997; Ram Krishna et al., 1997). The activated carbon has been the most widely used adsorbent for the removal of organic compounds from water. The other substances used as adsorbents for the removal of organic compounds from water are peats (Coupl et al., 1976), Iron(III) sorbed Zinc silicate and Iron(III) diethanolamine (Singh et al., 1987, 1988).

Aromatic amines are gaining importance in recent years owing to their industrial, pharmaceutical and toxicological applications. Several chromatographic methods have been reported for their identification and separation (Eaton et al., 1988; Evans et al., 1988; Dhillon et al., 1988). A considerable work has been reported from our laboratory for the identification and separation aromatic amines by thin layer chromatography (Ajmal et al., 1990, 1993).
The identification and determination of some aromatic amines at trace level by HPLC has been reported from our laboratory (Rao et al., 1999). However the determination of traces of aromatic amines in waters and wastewater requires sample concentration in order to reach their determination limits by HPLC. Adsorption is one of the most inexpensive and simple method for the removal and recovery of pollutants from large volume of water samples. Pyrolusite has been used earlier in our laboratory as an adsorbent for the removal of Pb(II) from wastewater (Ajmal et al., 1995). In this chapter the adsorption properties of pyrolusite have been compared with activated carbon. The desorption studies can be utilized for the recovery and preconcentration of aromatic amines before their determination in wastewater samples.

5.2 MATERIAL AND METHODS

5.2.1 Adsorbents:

Activated carbon and pyrolusite (125 mesh size, a manganese ore from kala Handi, Orissa, India) were used as adsorbents for the removal of aromatic amines from aqueous solution. The adsorbents were sieved to desired mesh size and then washed several times with distilled water and finally dried in an oven at 60°C.

5.2.2 Reagents and Samples:

Stock solution of aromatic amines (100 μg mL⁻¹) viz. aniline, α-naphthylamine, β-naphthylamine and diphenylamine (AR Grade) were prepared in methyl alcohol. All other chemicals used were of HPLC grade.
5.2.3 Apparatus:

High performance liquid chromatograph equipped with Shimadzu Spectrophotometric detector model SPD 6 AV, Pump LC 6A and system controller SCL 6B was used. Peak area and retention time was calculated with Shimadzu chromatopack C-R6A data processor (Shimadzu Scientific Instrument Inc. Japan).

5.2.4 Sample Analysis:

The analysis of aromatic amines was carried on 0.6 φ x 15 cm Shimpack CLC ODS (Shimadzu, Japan) column at room temperature using methyl alcohol and 0.1 M NaClO₄ mixture (80:2) as mobile phase with a flow rate of 0.5 ml min⁻¹. The effluent was monitored at 256 nm. The peaks were identified and quantified as described in our earlier paper (Rao et al., 1999).

5.2.5 Batch Adsorption Studies:

Batch adsorption studies were carried out by shaking 0.5 g of adsorbent with 50 ml aqueous solution of aromatic amine of desired concentration in stoppered conical flask for 24 hours. The mixture was then filtered and equilibrium concentration of aromatic amine in the filtrate was determined by HPLC by injecting a desired quantity of filtrate (5-20 μL) into the sample loop (200 μL capacity).

5.2.6 Adsorption Models:

To quantify the adsorption capacity of activated carbon and pyrolusite for the removal of aromatic amines from water, the Langmuir and Freundlich models were used.
5.2.7 Adsorption Studies in Non-Aqueous Medium:

Adsorption studies on both the adsorbents were also carried out in 100% methyl alcohol under similar condition in order to study the effect of solubility of aromatic amines. β-naphthylamine was chosen for this study.

5.2.8 Competitive Adsorption:

In order to study the effect of other aromatic amines on the adsorption of β-naphthylamine, a mixture of β-naphthylamine and diphenylamine was added and the adsorption behaviour was studied. β-Naphthylamine and diphenylamine were chosen because they can be separated and determined by HPLC method developed in our laboratory (Rao et al., 1999).

5.2.9 Desorption Studies:

Desorption studies were carried out by batch as well as column operations. In batch process 50 ml solution containing a mixture of β-NAM and DPAM was treated with 1 g adsorbent and after 24 hours it was filtered. The unadsorbed amines in the filtrate were determined by HPLC. The adsorbent was washed several times with distilled water. It was then transferred in another conical flask and treated with 20 ml solvent. The amount of aromatic amines desorbed was then determined again by HPLC.

In column operation, 0.5 g of the adsorbent was taken in a glass column (0.6 cm in diameter), washed several times with distilled water and then a desired quantity of amine was passed over the
adsorbent. The adsorbed amines were then eluted with an appropriate eluent with a flow rate of 0.5 ml min$^{-1}$. The effluent was collected in 10 ml fractions. The volume of effluent was reduced to 1 ml by evaporating it over a water bath. 20 μL of this sample was then injected in sample loop of HPLC for the determination of aromatic amine.

5.3 RESULTS AND DISCUSSION

The adsorption of various aromatic amines on activated carbon and pyrolusite are shown in Table 5.1. α-Naphthylamine, β-naphthyamine and diphenylamines are strongly adsorbed on activated carbon but the adsorption of aniline is least (15%).

The adsorption of β-naphthylamine and diphenylamine is maximum (95 and 100%) on pyrolusite while adsorption of aniline is negligible.

The effect of various initial concentration of α and β naphthylamine on both the adsorbents are summarized in Table 5.2 and 5.3.

Adsorption of α-Naphthylamine on activated carbon remains high and vary only from 100 to 95% when initial concentration is increased from 10 μg mL$^{-1}$ to 50 μg mL$^{-1}$, while adsorption on pyrolusite increases rapidly and reaches from 40% to 92% for the same variation in the initial concentration of α naphthylamine showing the increased efficiency of pyrolusite with increasing initial concentration.

The adsorption of β naphthylamine on activated carbon is found to be very high (100%) as compared to α naphthylamine over a wide
range of initial concentration (4 µg mL⁻¹ to 100 µg mL⁻¹) and after that % adsorption decreases slightly (99% to 96%), when initial concentration is further increased from 150 µg mL⁻¹ to 400 µg mL⁻¹. The adsorption behaviour of β naphthylamine on pyrolusite is different as compared to activated carbon. The % adsorption increases initially from 70% to 95% when initial concentration of β naphthylamine is increased from 4 µg mL⁻¹ to 20 µg mL⁻¹ but after that % adsorption decreases and reaches to (76%), when initial concentration is increased to 200 µg mL⁻¹.

The high adsorption of α and β naphthylamine on activated carbon and pyrolusite may be due to their limited solubilities in water. Aniline comparatively more soluble than naphthylamines shows least adsorption (Rai et al., 1988; Giusti et al., 1974). Since β NAM is sparingly soluble in water, one may expect its precipitation in aqueous medium. However the adsorption was not affected and remained high (97%) when both the adsorbents were treated separately with alcoholic solution of β NAM (Table 5.3).

The effect of various doses of activated carbon on the adsorption of β naphthylamine is shown in Fig. 5.1. The % adsorption increases from 96.5 to 99.5% when adsorbent dose is increased from 0.2g to 1.0g with an initial concentration of 400 µg mL⁻¹. However the adsorption behaviour of β naphthylamine on pyrolusite is more pronounced when adsorbent dose is increased from 0.2g to 3.0g with an initial concentration of 100 µg mL⁻¹. The effect of adsorbent doses on adsorption density (µg mL⁻¹g⁻¹) and % adsorption on both the
adsorbents is shown in Fig. 5.1 and 5.2. The adsorption density decreases when doses of activated carbon is increased and reaches to a value of 398 µg mL\(^{-1}\)g\(^{-1}\) while % adsorption increases and reaches to a maximum value of 99.5% at 1 g dose of activated carbon. A similar behaviour was observed on pyrolusite. The adsorption density decreases when adsorbent dose is increased and reaches to a value of 31.3 µg mL\(^{-1}\)g\(^{-1}\) while % adsorption increases and reaches to a maximum value of (94%) when pyrolusite dose is increased to 3g.

The decrease in adsorption density with increase in adsorbent dose on both the adsorbents indicates that some of the adsorption sites remains unsaturated when adsorbent dose is increased. However the adsorption density on activated carbon decreases from 100% to 79%, while on pyrolusite it decreases from 100% to 78% for the same quantity of adsorbent dose (1 gm).

5.3.1 Competitive Adsorption :

The adsorption behavior of β NAM on activated carbon and pyrolusite was studied in presence of other aromatic amines. Table 5.4 shows that adsorption of β NAM on both adsorbents remains unaffected in presence of DPAM over a wide range of initial concentrations (20 to 60 µg mL\(^{-1}\)).

5.3.2 Adsorption Isotherms :

The adsorption data has been analysed in the light of Langmuir and Freundlich adsorption models. The Langmuir equation may be described as
where $x$ = amount of adsorbate (μgs)

$m$ = amount of adsorbent (gms)

$x/m$ is adsorbate uptake per unit weight of adsorbent, $C_e$ is the equilibrium concentration (μg mL$^{-1}$). $\theta^0$ and $b$ are Langmuir constant relating to adsorption capacity and adsorption energy respectively.

The Freundlich equation may be described as

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e$$

where $C_e$ is the equilibrium concentration (μg mL$^{-1}$). $x/m$ is the amount adsorbed per unit weight of adsorbent. $K_f$ and $n$ are Freundlich constants. The isotherms are shown in Fig. 5.3 & 5.4 and 5.5 & 5.6. The adsorption of β NAM on activated carbon follows Langmuir and Freundlich equations but Freundlich equation is better obeyed by pyrolusite than Langmuir equation as it is evident from the values of regressions coefficients shown in Table 5.6. The Freundlich type behavior indicates the heterogeneous types of adsorption sites on pyrolusite. Further the values of Freundlich constant $K_f$ which is indicative of adsorption capacity, is much higher on activated carbon as compared to pyrolusite indicating that β NAM is strongly adsorbed on activated carbon. The values of $x/m$ for any given equilibrium concentration $C_e$ is also higher on activated showing that β NAM is strongly adsorbed on activated as compared to pyrolusite.
5.3.3 Desorption Studies:

The desorption of β NAM and DPAM (batch process) using different solvent is summarized in Table 5.5. It is evident from the table that the recovery of β NAM and DPAM from activated carbon is very poor when methyl alcohol and dilute NaOH are used as solvent. However, desorption is slightly increased when non-polar solvent (n hexane) is used. This behaviour shows that aromatic amines are very strongly adsorbed on activated carbon (as it is evident from other adsorption data) and difficult to desorb. Hence activated carbon can be used only for the removal of β NAM and DPAM from wastewater.

However, when pyrolusite is used as adsorbent under similar conditions the recovery of amines is much larger. This may be due to the fact that adsorption of aromatic amines on pyrolusite is not very strong as compared to activated carbon. This property of pyrolusite can be utilized advantageously for the recovery of aromatic amines using proper solvent. The desorption trend of β NAM on pyrolusite by column operation is shown in Fig. 5.7. Excellent results are obtained when a mixture of n-hexane and Isopropanol (99+1) is used as eluent. The recovery of β NAM is found to be 82.5%. It is also interesting to note that desorption is fast and maximum recovery is achieved (45%) within first fraction of the eluent. Pyrolusite, therefore, can be utilized for the preconcentration and recovery of traces of aromatic amines from wastewater.

5.4 CONCLUSION

Pyrolusite shows remarkable sorption capacity for DPAM and β NAM as compared to aniline; (the adsorption followed the order
Activated Carbon : - DPAM = β NAM > α NAM > Aniline

Pyrolusite : DPAM = β NAM > α NAM > Aniline

The maximum adsorption of β NAM occurred in the concentration range 4-20 μg mL⁻¹ on pyrolusite (95%) and 4-50 μg mL⁻¹ on activated carbon (100%). The effect of various doses of activated carbon on the adsorption of β NAM confirm Langmuir and Freundlich isotherms whereas Freundlich isotherm is obeyed by pyrolusite. The adsorption of β NAM on both the adsorbents is not affected in presence of DPAM over a wide range of their initial concentrations (20-60 μg mL⁻¹). The desorption studies of β NAM on pyrolusite was carried out by batch as well as column processes. Excellent results were obtained when a mixture of n-hexane and isopropanol (91:1) was used as eluent.
Table 5.1. Adsorption of Aromatic Amines

<table>
<thead>
<tr>
<th>Aromatic Amines</th>
<th>Initial Concentration ($\mu$g mL$^{-1}$)</th>
<th>Adsorption % Activated Carbon</th>
<th>Pyrolusite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>100</td>
<td>15%</td>
<td>00%</td>
</tr>
<tr>
<td>$\alpha$ NAM</td>
<td>100</td>
<td>100%</td>
<td>84%</td>
</tr>
<tr>
<td>$\beta$ NAM</td>
<td>100</td>
<td>99%</td>
<td>85%</td>
</tr>
<tr>
<td>DPAM</td>
<td>100</td>
<td>100%</td>
<td>85%</td>
</tr>
</tbody>
</table>

Table 5.2. Effect of Concentration on the Adsorption of $\alpha$ NAM

<table>
<thead>
<tr>
<th>Initial Concentration ($\mu$g mL$^{-1}$)</th>
<th>Adsorption % Activated Carbon</th>
<th>Pyrolusite</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>10</td>
<td>95%</td>
<td>40%</td>
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<td>20</td>
<td>95%</td>
<td>80%</td>
</tr>
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<td>40</td>
<td>95%</td>
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</tr>
<tr>
<td>50</td>
<td>96%</td>
<td>92%</td>
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Table 5.3. Effect of Concentration on the Adsorption of β NAM

<table>
<thead>
<tr>
<th>Initial Concentration (μg mL⁻¹)</th>
<th>Solvent</th>
<th>Adsorption %</th>
<th>Activated Carbon</th>
<th>Pyrolusite</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Water</td>
<td>100%</td>
<td>70%</td>
<td></td>
</tr>
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<td>76%</td>
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<tr>
<td>300</td>
<td>Water</td>
<td>95%</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>Water</td>
<td>96%</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Methanol</td>
<td>97%</td>
<td>97%</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4. Adsorption of β NAM in presence of DPAM on Activated Carbon and Pyrolusite

<table>
<thead>
<tr>
<th>Aromatic Amines</th>
<th>Initial Concentration (μg mL⁻¹)</th>
<th>Adsorption %</th>
<th>Activated Carbon</th>
<th>Pyrolusite</th>
</tr>
</thead>
<tbody>
<tr>
<td>β NAM</td>
<td>60</td>
<td>98%</td>
<td>87%</td>
<td></td>
</tr>
<tr>
<td>DPAM</td>
<td>60</td>
<td>100%</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>β NAM</td>
<td>20</td>
<td>--</td>
<td>96%</td>
<td></td>
</tr>
<tr>
<td>DPAM</td>
<td>20</td>
<td>--</td>
<td>100%</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.5. Recovery of Aromatic Amines from Activated Carbon and Pyrolusite by Batch process. Amount of Adsorbent = 1 g

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Aromatic Amine</th>
<th>Amount Loaded (μg)</th>
<th>Activated Carbon</th>
<th>Pyrolusite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Amount Adsorbed (μg)</td>
<td>Amount Recovered (μg)</td>
</tr>
<tr>
<td>1. Methyl Alcohol</td>
<td>β NAM</td>
<td>3000</td>
<td>3000</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>DPAM</td>
<td>3000</td>
<td>3000</td>
<td>40</td>
</tr>
<tr>
<td>2. 0.05 M NaOH</td>
<td>β NAM</td>
<td>3000</td>
<td>3000</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>DPAM</td>
<td>3000</td>
<td>3000</td>
<td>40</td>
</tr>
<tr>
<td>3. n-hexane</td>
<td>β NAM</td>
<td>3000</td>
<td>3000</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>DPAM</td>
<td>3000</td>
<td>3000</td>
<td>120</td>
</tr>
</tbody>
</table>
Table 5.6. Isotherm Parameters for the Adsorption of β NAM on Activated Carbon and Pyrolusite at room temperature

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$\frac{1}{\theta_0 b}$</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>0.9339</td>
<td>0.0042</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>0.8818</td>
<td>0.1139</td>
</tr>
</tbody>
</table>
Fig 5.1 Effect of Adsorbent doses (Activated Carbon)

Fig 5.2 Effect of adsorbent doses (Pyrolusite)
Fig 5.3 Langmuir Isotherm (Activated Carbon)

Fig 5.4 Freundlich Isotherm (Activated Carbon)
Fig. 5.5 Langmuir Isotherm (Pyrolusite)

Fig. 5.6 Freundlich Isotherm (Pyrolusite)
Fig. 5.7 Elution of β Naphthyl amine on Pyrolusite
REFERENCES


Rifaqat Ali Khan Rao, M. Ajmal, B.A. Siddiqui and Shamim Ahmad; Separation and determination of trace levels of aromatic amines by HPLC. Environmental Monitoring and Assessment 1999, 54, 289-299.


Conclusion & Future Perspectives
CONCLUSION AND FUTURE PERSPECTIVES

The use of the economically viable adsorbents such as teak leaves, fruit peel of orange and pyrolusite for the treatment of industrial waste may be of interest to small and medium industries. Initial construction and operational costs of conventional wastewater treatment plants are the most significant factors in the selection of process technology. The cost to small and medium size industries for achieving the same level of wastewater treatment as large industries using standard technology is disproportionately high.

The above materials have been found good adsorbent for the removal of heavy metals and organic compounds from synthetic and industrial wastewater. In present study our main thrust area was to explore the adsorption properties of various low cost adsorbents. The second task was to study the extent of removal and recovery of heavy metals from electroplating wastewater on laboratory scale. Now our next step is to apply these finding on industrial wastewater at large scale.

In the next stage, the electroplating wastewater samples will be collected from various units and they will be analysed in details. The total volume of wastewater discharge per day from these units will be found out and then the total amount of adsorbent required will be calculated. The work will also be extended for the recovery of these metal ions so that they can be reutilized in the electroplating plants, since these inexpensive materials are available abundantly in Aligarh and a large number of small and medium class electroplating plants are operating in this town.
LIST OF PUBLICATION


