Chapter–I

INTRODUCTION

Water is the most essential requirement in daily life along with air. Though eighty percent of the earth’s surface is covered by water, but only small part is available for drinking, agriculture, domestic and industrial purpose. Water pollution occurs due to the presence of dissolved inorganic, organic and other substances in addition to the physical factors such as turbidity, color, temperature of effluent, associated radioactivity etc. Organic pollution may be due to proteins, fats and carbohydrates. Alkalis, acids, inorganic salts and other chemicals formed during processing lead to inorganic pollution. These chemicals corrode the metals and are toxic. Paper and pulp, tannery, textile and coke oven industries discharge these chemicals. Inorganic chemicals such as free chlorine, ammonia, hydrogen sulfide and other sulfides, salts of metals like Cr, Ni, Zn, Cd, Cu, Ag etc are usually found in metal plating liquid wastes, alkaline producing units, polyvinyl chloride, coke oven and fertilizer industries. Chromates, phosphates, ammonia and urea are typical chemicals found in effluents from fertilizer industries [1].

At present, only about ten percent of the polluted water generated is treated and the remaining untreated polluted water is discharged into our water bodies like ground water, rivers etc. Such contaminated water carries disease-causing microbes, chemicals and heavy metals. The harmful effects of these pollutants have been known since long, but it is only in the recent years that public concern has led to the strict legislative laws governing the discharge of toxic pollutants. In view of the above problems, Pollution Act, 1990 has laid stringent rules for environment protection which states that source reduction is more desirable that
waste management and pollution control. This act has provisions for controlling
pollution caused by industries or communities so as to meet the minimum
standards for any function and purpose.

**Heavy metal pollution**

Due to rapid industrialization, the toxic metal pollution is increasing causing
destabilization in ecosystem. Toxic heavy metals include chromium, cadmium,
mercury, silver, lead and tin, although several nutrient metals, notably zinc,
copper and nickel, can also be toxic at elevated concentrations. Trace metals are
of environmental interest both as limiting nutrients and as toxins. If not properly
managed, the industrial waste water is responsible for severe damage to the
environment and adversely affecting the health of the people. Some of the heavy
metal effluents discharged by different industries are shown below in Table-1.1.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Heavy metals present in effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloro-alkali</td>
<td>Cr, Cd, Cu, Pb, Zn, Hg, Se</td>
</tr>
<tr>
<td>Paints and dyes</td>
<td>Cr, Cd, Cu, Pb, Zn, Se</td>
</tr>
<tr>
<td>Petroleum refinery</td>
<td>Cr, Cd, Cu, Pb, Zn</td>
</tr>
<tr>
<td>Fertilizers</td>
<td>Cr, Cd, Cu, Pb, Zn, Hg, Mn, As</td>
</tr>
<tr>
<td>Motor vehicles</td>
<td>Cr, Cd, Pb, Zn, Hg, Se</td>
</tr>
<tr>
<td>Mining and metallurgy</td>
<td>Cr, Cd, Cu, Zn, Hg, Se, As</td>
</tr>
</tbody>
</table>

Heavy metals that affect the human organs are shown below in Table-1.2.
Table-1.2
Effect of pollutants on human organs

<table>
<thead>
<tr>
<th>Heavy metal pollutants</th>
<th>Target organ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>Stomach, lower respiratory system, skin and lungs</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Liver, kidneys and bones</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Blood, kidneys, bones and teeth</td>
</tr>
<tr>
<td>Nickel</td>
<td>Intestines</td>
</tr>
<tr>
<td>Lead</td>
<td>Blood, brain, bones, kidneys and teeth</td>
</tr>
<tr>
<td>Mercury</td>
<td>Blood and kidneys</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Blood and kidneys</td>
</tr>
</tbody>
</table>

Of these heavy metals, chromium and cadmium represent a major toxic pollutant that calls for special attention.

**Chromium (Cr)**

Chromium was discovered by Louis Nicolas Vauquelin in the mineral crocoite (*lead chromate*) in 1797. Chromium is a naturally occurring element found in rocks, animals, soil, volcanic dust and gases. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odourless, tasteless, and malleable. Chromium is the 24th most abundant element in earth's crust with an average concentration of 100 ppm [2]. The concentrations range is between 1 and 3000 mg/kg in soil, 5 to 800 µg/L in sea water and 26 µg/L to 5.2 mg/L in rivers and lakes [3]. The most common forms present in the environment are trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)].
The relation between Cr (III) and Cr (VI) strongly depends on pH and oxidative properties of the location. Chromium is regarded with great interest because of its high corrosion resistance and hardness.

**Uses of chromium**

- used in yellow pigment, chrome red, chrome green [4]
- used in stainless steel, made of iron with 10% nickel and 18% chromium is widely used in cookware and cutlery
- used in leather tanning [5]
- used as oxidizing agent and for cleaning purposes
- used as gasoline additive [6]
- used in Phillips catalysts [7]

**Sources of chromium contamination and health hazards**

Chromium has been considered as sixteenth toxic pollutant. It has become a serious health concern due to its carcinogenic and teratogenic characteristics [8]. Water insoluble chromium (III) compounds and chromium metal are not considered a health hazard. Chromium contamination is chromite ore refining, ferrochromium production, refractory production chromium chemicals production, steel production, leather tanning, coal and oil combustion, cement production, municipal refuse and sewage sludge incineration, cooling towers, coke ovens etc.

The acute toxicity of chromium (VI) is due to its strong oxidational properties. After it reaches the blood stream, it damages the kidneys, the liver and blood cells through oxidation reactions. Hemolysis, renal and liver failure are the results of these damages. Aggressive dialysis can improve the situation [9]. Contact with
products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers [10]. The carcinogenity of chromate dust is known for a long time, and in 1890 the first publication described the elevated cancer risk of workers in a chromate dye company [11, 12]. Accidental swallowing of larger amounts of Cr (VI) causes convulsions, stomach upset and damage of kidneys and liver. Exposure for a longer period leads to skin ulcer. Humans that breathe high levels (greater than 2 μg/m³) can cause respiratory irritation and in animals, the ability to fight diseases lowers.

**Tolerance limits of chromium**

The allowable chromium concentrations specified for different purposes are given below. Several methods are available for the removal of metals from industrial effluents to the prescribed tolerance limits. These include precipitation, cementation, ion exchange, reverse osmosis, evaporation, electro dialysis, adsorption and biosorption.

<table>
<thead>
<tr>
<th>Source of water</th>
<th>Tolerance limit, mg/L</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>0.05</td>
<td>IS-10500</td>
</tr>
<tr>
<td>Inland surface water</td>
<td>2.0</td>
<td>IS-10500</td>
</tr>
<tr>
<td>Public sewers</td>
<td>2.0</td>
<td>IS-10500</td>
</tr>
<tr>
<td>Marine coastal areas</td>
<td>2.0</td>
<td>IS-10500</td>
</tr>
</tbody>
</table>
Cadmium (Cd)

Cadmium is a group 12 element discovered in 1818 [13] and was first extracted commercially in 1886 in Silesia. The metal was named after the Latin word ‘calamine’ and greek ‘kadmaa’. Cadmium is naturally formed element ((0.1 -0.5 µg/g). Greenokite (CdS) is the only mineral of any consequence bearing cadmium.

Cadmium is most often associated in small quantities with zinc ores, such as sphalerite (ZnS). Almost all cadmium is obtained as a by-product in the treatment of zinc, copper and lead ores. Small amounts of cadmium (10 %) are produced from secondary sources, mainly from dust generated by recycling iron and steel scrap. As alloying element, it has antifriction properties and lowers the melting point of certain metals such as lead, tin, antimony, bismuth and zinc. It is a ductile, malleable, soft, silver-white that can be easily scratched.

Uses of cadmium

- used in Ni-Cd batteries and other batteries
- used in cadmium pigments like yellow pigment, red pigment (cadmium red)
- used in cadmium stabilizers
- used in cadmium electroplating eg. Aircraft industry
- used as cadmium alloys [14]
- used in color television picture tubes [15]
- used as photoconductive surface coating for photocopier drums
- used in medicine as cadmium iodide [16]
Sources of cadmium contamination and health hazards

It is estimated that half of the cadmium in landfills comes from discarded Ni-Cd batteries. In the case of municipal incineration of household wastes, 30% of the metal feed of incinicators may come from spent batteries in municipalities where no recycling programs exist. Cadmium concentrations generally range from 5-15 mg/L in municipal waste and 50-1000 mg/L in incinerator fly ash. The cadmium is present in non-ferrous metals (zinc, lead and copper), iron and steel, fossil fuels (coal, oil, gas, peat and wood), cement and phosphate fertilizers as an impurity.

In the environment, cadmium is highly toxic to human, plant and animals. It represents a major hazardous waste that can be taken into the body through the pulmonary system from the contaminated air or cigarette smoke or via the digestive system through water or food contamination from plant cadmium uptake.

Cadmium ill effects:

Inhalation of cadmium-containing fumes can result initially in metal fume fever but may progress to chemical pneumonitis, pulmonary edema, and death [17]. Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache. Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and the kidneys.

Cadmium can cause hyperson, emphysema, renal cancer, prostrate cancer, kidney disease and human carcinogen. The bones become soft (osteomalacia), lose bone mineral density (osteoporosis) and become weaker. This causes the pain in the
joints and the back, and also increases the risk of fractures. In extreme cases of cadmium poisoning, mere body weight causes a fracture.

The kidneys lose their function to remove acids from the blood in proximal renal tubular dysfunction creates low phosphate levels in the blood (hypophosphatemia), causing muscle weakness and sometimes coma. Tobacco smoking is the most important single source of cadmium exposure in the general population. It has been estimated that about 10% of the cadmium content of a cigarette is inhaled through smoking.

**Tolerance limits of cadmium**

The allowable cadmium concentrations specified for different purposes are given below. Precipitation, cementation, ion exchange, reverse osmosis, evaporation, electro dialysis, adsorption and biosorption are the different methods available for the removal of metals from industrial effluents to the prescribed tolerance limits.

<table>
<thead>
<tr>
<th>Source of water</th>
<th>Tolerance limit, mg/L</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inland surface water</td>
<td>2.0</td>
<td>IS-10500</td>
</tr>
<tr>
<td>Drinking water</td>
<td>&lt; 0.01</td>
<td>IS-10500</td>
</tr>
<tr>
<td>Public sewers</td>
<td>1.0</td>
<td>IS-10500</td>
</tr>
<tr>
<td>Marine coastal areas</td>
<td>2.0</td>
<td>IS-10500</td>
</tr>
</tbody>
</table>
Aim and objective of the present investigation

The aim of this investigation is to develop abundantly available, efficient and inexpensive biosorbent for toxic heavy metal ion biosorption.

The main objectives of this investigation are:

1. Metal sample preparation (chromium and cadmium)
2. To characterize (FTIR, XRD & SEM analysis) the biosorbents: *Syzigium cumini* (java) seed powder and green algae (*Caulerpa taxifolia*)
3. To experimentally quantify the metal uptake by batch operation varying physicochemical conditions, such as
   - Agitation time
   - pH
   - Initial metal concentration
   - Biosorbent dosage
   - Temperature
4. Modeling by statistical experimental design using Response Surface Methodology as per the following steps:
   - The selection of independent variables of maximum effects on the system through screening studies.
   - The choice of the experimental design and carrying out the experiments according to the selected experimental matrix.
   - The mathematical-statistical treatment of the obtained experimental data through the fit of a polynomial function.
   - The evaluation of the model’s fitness.
5. Kinetic studies
6. Isotherm models
7. Evaluation of thermodynamic parameters
8. Column studies
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