1. Environmental Pollution

Pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. This occurs “when only short term economic gains are made at the cost of long term ecological benefits for humanity”. No phenomenon has led to greater ecological changes than has been made by mankind. During the last few decades we have contaminated our air, water and land on which life itself depends with a variety of waste products\(^1\). Pollution can take the form of chemical substances or energy, such as noise, heat, or light. Pollutants, the elements of pollution, can be foreign substances or energies, man made or naturally occurring; when naturally occurring, they are considered contaminants when they exceed natural levels.

1.1 Major forms of pollution

1.1.1 Air pollution

Air pollution is the release of chemicals and particulates into the atmosphere. Common gaseous air pollutants include carbon monoxide, sulphur dioxide, chlorofluorocarbons (CFCs) and nitrogen oxides produced by industry and motor vehicles. Photochemical ozone and smog are created when nitrogen oxides and hydrocarbons react with sunlight. Particulate matter, or fine dust is characterized by its micrometre size 2.5 to 10 pm.

1.1.2 Light pollution

Light pollution, includes light trespass, over-illumination and astronomical interference.

1.1.3 Noise pollution

Noise pollution, which encompasses roadway noise, aircraft noise, industrial noise as well as high-intensity sonar.
1.1.4 Soil pollution

Soil contamination occurs when chemicals are released intentionally, by spill or underground leakage. Among the most significant soil contaminants are hydrocarbons, heavy metals, herbicides, pesticides and chlorinated hydrocarbons.

1.1.5 Radioactive pollution

Radioactive contamination, resulting from 20th century activities in atomic physics, such as nuclear power generation and nuclear weapons research, manufacture and deployment.

1.1.6 Thermal pollution

Thermal pollution, is a temperature change in natural water bodies caused by human influence, such as use of water as coolant in a power plant.

1.1.7 Visual pollution

Visual pollution, which can refer to the presence of overhead power lines, motorway billboards, scarred landforms (as from strip mining), open storage of trash or municipal solid waste.

1.1.8 Water pollution

Water pollution, by the discharge of waste water from commercial and industrial waste (intentionally or through spills) into surface waters; discharges of untreated domestic sewage, and chemical contaminants like heavy metals such as lead, mercury, nickel, copper, cadmium, chromium etc., and textile synthetic dyes like malachite green, rhodamine-B, methylene blue, congored, crystal violet, acid blue etc.,

1.2 Pollution by heavy metals

Water is essential for survival. But today about 200 million people in India do not have access to safe drinking water due to water pollution. Any change in physical, chemical or biological properties of water is known as water pollution. Heavy metals and dyes plays an important role in water pollution. Heavy metals are
continuously released into the aquatic eco-system from natural process such as volcanic activity and weathering of rocks. The effluents from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing metal loads in the water bodies. The heavy metal contamination of the water system is responsible for serious diseases and death. Waste water containing heavy metal pollutants like lead, mercury, nickel, copper, cadmium and chromium causes direct toxicity, both to human and other living organisms due to their presence beyond specified limits. The presence of toxic heavy metals in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies, is one of the most important environmental issues. Their presence in aquatic ecosystem poses human health risks and causes harmful effect to living organisms. In this study, three heavy metals namely lead, nickel and chromium are used for their removal. The following paragraphs will highlight the importance, applications and hazards of them.

1.2.1 Lead

Lead is known to be one of the heavy metals and widely used in many industrial applications. Lead is a soft, malleable metal. Metallic lead has a bluish-white colour after being freshly cut, but it soon tarnishes to a dull grayish colour when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid. The permissible limit for Pb(II) in waste water, as given by Environmental protection Agency (EPA), is 0.05 mg/L and that of Bureau of Indian standards (BIS) is 0.01 mg/L.

<table>
<thead>
<tr>
<th>Table 1.1 Properties of lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>General properties</td>
</tr>
<tr>
<td>Name, symbol, atomic number</td>
</tr>
<tr>
<td>Element category</td>
</tr>
<tr>
<td>Group, period, block</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Standard atomic weight</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Electron configuration</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Heat of vapourization | 179.5 kJmol$^{-1}$ |
Applications

Lead is used in building construction, lead-acid batteries, bullets and shots, weights, as part of solders, pewters, fusible alloys and as a radiation shield. Lead has the highest atomic number of all of the stable elements, so it is used in electroplating, metal finishing, textile industries, storage batteries, pigments, as fuel, photographic materials and explosive manufacturing.\(^6\)

Hazards

Lead, at certain exposure levels, is a poisonous substance to living organisms. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. Like the element mercury, another heavy metal, lead is a neurotoxin that accumulates both in soft tissues and in the bones. Lead is highly toxic as its presence in drinking water above the permissible limits causes adverse health effects such as anemia, hepatitis, nephritic syndrome and renal damages. The permissible limit for Pb in water according to WHO (1985) is 0.05 mg/L.

1.2.2 Nickel

Nickel is the heavy metal which has been widely used in electroplating industry. It is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile. Pure nickel shows a significant chemical activity, though larger collections of the metal are slow to react with air at ambient conditions due to the formation of a protective oxide film. The permissible limit for Ni(II) in waste water as given Bureau of Indian standards (BIS) is 0.02 mg/L.

Table 1.2 Properties of nickel

<table>
<thead>
<tr>
<th>General properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name, symbol, atomic number</td>
<td>nickel, Ni, 28</td>
</tr>
<tr>
<td>Element category</td>
<td>transition metal</td>
</tr>
<tr>
<td>Group, period, block</td>
<td>10, 4, d</td>
</tr>
<tr>
<td>Standard atomic weight</td>
<td>58.6934</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Ar] 4s(^2) 3d(^8)</td>
</tr>
<tr>
<td>Phase</td>
<td>solid</td>
</tr>
<tr>
<td>Density (near r.t.)</td>
<td>8.908 g cm(^{-3})</td>
</tr>
<tr>
<td>Melting point</td>
<td>1728 K</td>
</tr>
<tr>
<td>Boiling point</td>
<td>3186 K</td>
</tr>
<tr>
<td>Heat of vapourization</td>
<td>377.5 kJmol(^{-1})</td>
</tr>
</tbody>
</table>
Applications

The fraction of global nickel production presently used for various applications is as follows: 60% is used for making nickel steels, 14% is used in nickel-copper alloys and nickel silver, 9% is used to make malleable nickel, nickel clad, inconel and other superalloys, 6% is used in plating, 3% is used for nickel cast irons, 3% is used in heat and electric resistance alloys such as nichrome, 2% is used for nickel brasses and bronzes with the remaining 3% of the nickel consumption is used in all other applications combined. Nickel is used in many specific and recognizable industrial and consumer products, including stainless steel, alnico magnets, coinage, rechargeable batteries, electric guitar strings, microphone capsules, and special alloys.

Hazards

If waste water contaminated with divalent nickel is discharged to water ways without adequate treatment, soil and water resources become polluted. Electroplating is considered a major polluting industry because it discharges toxic materials and heavy metals through waste water (effluents). It is harmful to humans and other living organisms. Inhalation of divalent nickel causes an increase in the incidence of lung cancer. Moreover, soluble nickel compounds are carcinogenic, giving rise to cancers of the nasal cavities, lungs and other organs such as stomach and kidney. The main symptoms of nickel poisoning include headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness. World Health Organization, WHO has suggested that the maximum amount of nickel in drinking water should be 0.1 mg/L. But in many electroplating effluent water it is as high as 50 mg/ L.

1.2.3 Chromium

Chromium is one of the toxic contaminants, which exists in hexavalent and trivalent forms. Hexavalent form is more toxic than trivalent form and requires more concern. Chromium was regarded with great interest because of its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium to form
stainless steel. The main sources of chromium(VI) are tannery, paint, ink, dye, and aluminium manufacturing industries. Several International Environmental Agencies have introduced strict regulations with regard to metal discharge, especially from industrial activities. According to USEPA, the discharge of Cr(VI) and its other forms is regulated\textsuperscript{13} to below 2 mg/ L.

**Table 1.3 Properties of chromium**

<table>
<thead>
<tr>
<th>General properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name, symbol, atomic number</td>
<td>chromium, Cr, 24</td>
</tr>
<tr>
<td>Element category</td>
<td>transition metal</td>
</tr>
<tr>
<td>Group, period, block</td>
<td>6, 4, d</td>
</tr>
<tr>
<td>Standard atomic weight</td>
<td>51.9961</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Ar] 3d\textsuperscript{5} 4s\textsuperscript{1}</td>
</tr>
<tr>
<td>Phase</td>
<td>solid</td>
</tr>
<tr>
<td>Density (near r.t.)</td>
<td>7.19 g cm\textsuperscript{−3}</td>
</tr>
<tr>
<td>Melting point</td>
<td>2180 K</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2944 K</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>339.5 kJ mol\textsuperscript{−1}</td>
</tr>
</tbody>
</table>

**Applications**

The applications of chromium are numerous Chrome plating (electroplating with chromium) is currently the highest-volume use of the metal. Chromium and ferrochromium are produced from the single commercially viable ore, chromite, by silicothermic or aluminothermic reaction or by roasting and leaching processes. Trivalent chromium (Cr(III)) is required in trace amounts for sugar and lipid metabolism and few cases have been reported where its complete removal from the diet has caused chromium deficiency.

**Hazards**

In larger amounts and different forms, chromium can be toxic and carcinogenic. Exposure to Cr(VI) causes cancer in digestive tract and lungs\textsuperscript{14} and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage\textsuperscript{15}. Abandoned chromium production sites often require environmental clean up.

**1.3 Pollution by dyes**

A safe potable drinking water is necessary for every human being. Due to over population, India is suffering from persistent demand for safe drinking water. Dye and dye intermediates industries are the largest sector of chemical industries in India, since
they are used in textile, paints, pulp and paper industries. More than 80% of their production is utilized by the textile industries. A huge amount of water is necessary by these industries for the cleaning and washing purposes and they discharge highly coloured effluent containing different dyes. The highly coloured effluent upsets the biological processes. Unless properly collected, treated and disposed of, such type of waste water create serious water pollution problems. Among many synthetic dyes, congo red, malachite green and methylene blue removal are studied in this study. The following paragraphs will highlight the importance, applications and hazards of dyes.

1.3.1 Congo red

Congo red is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid (formula: C$_{32}$H$_{22}$N$_{6}$Na$_{2}$O$_{6}$S$_{2}$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol. It has a strong, though apparently non-covalent, affinity to cellulose fibres.

![Figure 1.1 Structure of congo red](image)

**Table 1.4 Properties of congo red**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Identifiers</th>
<th>CAS number</th>
<th>PubChem</th>
<th>ChemSpider</th>
</tr>
</thead>
<tbody>
<tr>
<td>IUPAC name</td>
<td>sodium sodium 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulphonate)</td>
<td></td>
<td>573-58-0</td>
<td></td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C$<em>{32}$H$</em>{22}$N$<em>{6}$Na$</em>{2}$O$<em>{6}$S$</em>{2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar mass</td>
<td>696.665</td>
<td></td>
<td>11313</td>
<td>10838</td>
</tr>
</tbody>
</table>
Applications

Though the use of congo red in the cellulose industries (cotton, textile, wood pulp & paper) has long been abandoned, primarily because of its tendency to change color when touched by sweaty fingers, to run, and because of its toxicity but still they are employed in some places by ignoring all its ill-effects. Congo red dye is a synthetic, reactive, water soluble dye, used in medicine (as a biological stain) and as an indicator since it turns from red-brown (in basic medium) to blue in acidic one. It is also used to color textiles (initially cotton). It could also be used in gamma-ray dosimeter since its colour decays with the intensity of their radiation.

Hazards

There are numerous symptoms that are associated with this dye. The most common ones have to do with the heart, such as heart failure, arrhythmia, and an irregular heart beat. Also respiratory tract can be affected and cause hemoptysis. Usually the spleen enlarges and sometimes ruptures. The gastrointestinal tract is usually affected and causes vomiting, hemorrhaging and diarrhea. Amyloidosis can also affect the motor functions and cause polyneuropathy. When the amyloid fibrils and oligomers get to the skin they can cause skin lesions. One of the most famous symptoms is macroglossia.16

1.3.2 Malachite green

Malachite green is classified in the dyestuff industry as a triarylmethane dye. Formally, malachite green refers to the chloride salt \([C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl\), although the term malachite green is used loosely and often just refers to the coloured cation. The oxalate salt is also marketed. The chloride and oxalate anions have no effect on the colour. The intense green colour of the cation results from a strong absorption band at 620 nm (extinction coefficient of \(10^5 \text{ M}^{-1}\text{cm}^{-1}\)).

![Structure of malachite green](image)

Figure 1.2 Structure of malachite green
Table 1.5 Properties of malachite green

<table>
<thead>
<tr>
<th>Properties</th>
<th>Identifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>IUPAC name</td>
<td>4-[(4-dimethylaminophenyl) phenyl-methyl]-N,N-dimethylaniline</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C_{23}H_{25}ClN_{2} (chloride)</td>
</tr>
<tr>
<td>Molar mass</td>
<td>364.911 g/mol (chloride)</td>
</tr>
</tbody>
</table>

Applications

Malachite green (MG) is traditionally used as a dye for materials such as silk, leather, and paper. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose. MG is active against a oomycete Saprolegnia, which infects fish eggs in commercial aquaculture. It is also popular treatment against ichthyophthirius in freshwater aquaria. It is an organic compound that is used as a dyestuff and has emerged as a controversial agent in aquaculture. Numerous niche applications exploit the intense colour of MG. It is used as a biological stain for microscopic analysis of cell biology and tissue samples. In the Gimenez staining method, basic fuchsin stains bacteria red or magenta, and malachite green is used as a blue-green counter stain. It can also directly stain endospores within cells; here a safranin counter stain is often used.

Hazards

Malachite green is highly cytotoxic to mammalian cells and also acts as a liver tumor-enhancing agent. Human fed malachite green experience “a dose-related increase in liver DNA adducts” along with lung adenomas. Leuco-malachite green causes an “increase in the number and severity of changes”. As leuco-malachite green is the primary metabolite of malachite green and is retained in fish muscle much longer, most intake of malachite green would be in the leuco form. Therefore it could be concluded that malachite green caused carcinogenic symptoms, but a direct link between malachite green and liver tumor was not established. ¹⁷

1.3.3 Methylene blue

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula C_{16}H_{18}N_{3}SCl. It has many uses in a range of different fields, such as biology
and chemistry. At room temperature it appears as a solid, odourless, dark green powder, that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of methylene blue.¹⁸

![Figure 1.3 Structure of methylene blue](image)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Identifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>IUPAC name</td>
<td>CAS number</td>
</tr>
<tr>
<td>3,7-bis(Dimethylamino)-phenothiazin-5-i um chloride</td>
<td>61-73-4</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>PubChem</td>
</tr>
<tr>
<td>C₁₆H₁₈N₃SCl</td>
<td>6099</td>
</tr>
<tr>
<td>Molar mass</td>
<td>ChemSpider</td>
</tr>
<tr>
<td>319.85 g/mol</td>
<td>5874</td>
</tr>
</tbody>
</table>

**Applications**

Methylene blue is widely used as a redox indicator in analytical chemistry and is also a photosensitizer used to create singlet oxygen when exposed to both oxygen and light. It is used in this regard to make organic peroxides by a Diels-Alder reaction which is spin forbidden with normal atmospheric triplet oxygen. In biology, methylene blue is used as a dye for a number of different staining procedures, such as Wright's stain and Jenner's stain. Since it is a temporary staining technique, methylene blue can also be used to examine RNA or DNA under the microscope or in a gel. It can also be used as an indicator to determine if a cell, such as yeast, is alive or not.

**Hazards**

Important side effect of methylene blue are nausea, stomach upset, diarrhoea, vomiting and bladder irritation. This medication may cause the urine or stool to turn green-blue. Very serious side effects of methylene blue are dizziness, fainting, high fever, fast/irregular/pounding heartbeat, pale/blue skin color, unusual tiredness. Immediate medical attention should be sought if these very serious side effects occur:
chest pain, including rash, itching/swelling (especially of the face/tongue/throat), severe dizziness and trouble breathing.

### 1.4 Need for removal of heavy metals and dyes from environment

It is essential to remove metal ions and dyes from industrial wastewater before discharging into natural water sources to meet National Regulatory Standards as well as to protect public health.

#### 1.4.1 The conventional methods for removing heavy metals and dyes

The conventional methods for removing heavy metals and dyes from waste waters include chemical precipitation, electrochemical treatment, evaporation, ion exchange, membrane processing, vapouration, and solvent extraction. However, the application of these treatment processes has been found to be sometimes restricted, because of expensive investment, operational costs and the potential generation of secondary pollution. Furthermore such processes may be ineffective or extremely expensive when the initial heavy metal concentrations are in the range of 10-100 mg/L. In recent years, biosorption has been studied extensively using biomass as a biosorbent for heavy metals and dyes removal.

#### 1.4.2 Adsorption

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

#### 1.4.3 Advantages of adsorption

Adsorption process, proved its advantage over the other processes because of its

(1) ease of operation

(2) low maintenance costs
(3) high removal efficiency

(4) low energy requirements

(5) generation of no toxic slurries.

1.4.4 Adsorbents

Adsorbent is a material that sorbs another substance; i.e. that has the capacity or tendency to take up by either absorption or adsorption. Table 1.7 will give a vivid picture about the adsorbents and their applications.

Table 1.7 Some of examples of adsorbents and their applications

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbons</td>
<td>Removal of metal ions and dyes, Nitrogen from air, Hydrogen from syngas, Ethene from methane and hydrogen, Vinyl chloride monomer (VCM) from air, Removal of odours from gases, Recovery of solvent vapours, Removal of SOX and NOX, Purification of helium, Clean-up of nuclear off-gases, Water purification</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>Drying of gases, refrigerants, organic solvents, transformer oils, Desiccant in packings and double glazing Dew point control of natural gas</td>
</tr>
<tr>
<td>Activated Alumina</td>
<td>Drying of gases, organic solvents, transformer oils, Removal of HCl from hydrogen, Removal of fluorine in alkylation process</td>
</tr>
<tr>
<td>Polymers &amp; Resins</td>
<td>Water purification, Recovery and purification of steroids, amino acids, Separation of fatty acids from water and toluene, Separation of aromatics from aliphatics, Recovery of proteins and enzymes, Removal of colours from syrups, Removal of organics from hydrogen peroxide</td>
</tr>
<tr>
<td>Clay</td>
<td>Treatment of edible oils, Removal of organic pigments, Refining of mineral oils, Removal of polychlorinated biphenyls (PCBs)</td>
</tr>
<tr>
<td>Zeolites</td>
<td>Removal of oxygen from air, Drying of gasses, Removing water from zeotropes, Sweetening sour gases and liquids, Purification of hydrogen, Separation of ammonia and hydrogen, Recovery of carbon dioxide, Separation of oxygen and argon, water purification</td>
</tr>
</tbody>
</table>
1.4.5 Adsorbents used in this study

In this study, two selected natural seaweeds namely Valoria bryopsis and Enteromorpha were used as adsorbents for the removal of heavy metals namely lead, nickel and chromium and for the removal of dyes namely congo red, malachite green and methylene blue. These two natural seaweeds were collected from Kodiyakkarai and Tharangambadi coast of Tamil Nadu, in south east coast of India.

Three heavy metal ions (namely Cr$^{6+}$, Pb$^{2+}$ and Ni$^{2+}$) and three synthetic dyes (congo red, malachite green and methylene blue) were used as adsorbates for this study.

1.5 Aim and Scope of the present study

The present study therefore is envisaged to develop an effective method for the removal of metals/dyes from an aqueous solution by using the carbons prepared from the seaweeds (Valoria bryopsis and Enteromorpha). A large number of materials have been reported to trap metal ions and dyes through physisorption by many scientific workers. Several factors like residual toxicity, slow pace of the process, cost factor, unavailability, and rational loss cause serious setback in their suitability as agreed adsorbents.

This investigation aims at the identification of suitable naturally available seaweeds capable of meeting the above criteria. Though few materials which are biodegradable, cheap, indigenous, easy and safe to handle and redeemable were examined for their ability to reduce metal ion and dye pollution through physisorption or chemisorption, only naturally available seaweeds and their acid activated carbons have found to possess excellent adsorption ability and meet the above requirements satisfactorily. Besides the appreciable adsorption capacity the carbons are found to be non-toxic, abundant, eco-friendly and adaptable to laboratory conditions.

In this background, it was decided to investigate the approachability of the important indigenous, naturally available seaweed activated carbon to reduce the concentration of metal ions and dyes. Investigations to define the role of factors like, dosage, contact time, pH, concentration, temperature on the sorption ability, dynamics of equilibrium, nature of adsorption and effect of co-ions were included in the scope of
this work. The main objective of this investigation is to establish the suitable conditions for the best sorptive capacity of Valoria bryopsis and Enteromorpha in the removal of the metal ions/dyes